SYNTHESIS AND STUDY OF FLUORINATED THIOPHENES, BITHIOPHENES AND TRITHIOPHENES: MODELS FOR THE POLYMERIC MATERIAL

by

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Finally, my heartfelt thanks goes out to my family, for their support and motivation.

December 3, 2008

ABSTRACT

SYNTHESIS AND STUDY OF FLUORINATED THIOPHENES AND BITHIOPHENES, A MODEL FOR THE POLYMERIC MATERIAL

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The University of Texas at Arlington, 2008

Supervising Professor: Martin Pomerantz

The synthesis of 3-fluorothiophene was accomplished in four steps and 49% overall yield by a very convenient method. 2,5-Dibromo-3-fluorothiophene was prepared in essentially one step synthesis involving a decarboxylation-bromination reaction. Both 3-fluorothiophene and 2,5-dibromo-3-fluorothiophene are potential monomers for a wide variety of fluorinated polythiophenes.

Fluoroalkyl thiophene monomers, dimers and trimers were prepared. 3-Heptanoylthiophene is a key intermediate in the synthesis of the fluorinated monomers, dimers and polymers. The synthesis of 3-heptanoylthiophene by the reversible umpolung methodology was accomplished. This methodology has several advantages over the Grignard method such as: no undesirable byproducts were formed, cleaner and

straightforward reactions, easier purification process and improved overall yield. The synthesis of 3-(1,1-difluoroheptyl)thiophene and 2,5-dibromo-3-(1,1-difluoroheptyl)thiophene were accomplished. These are interesting monomers which are upon polymerization they could lead to novel conducting polymers. The monomer contains alkyl side chain that renders the corresponding polymer soluble in organic solvents, which is necessary for the processing of the polymer. The fluorinated polymer is anticipated to have remarkable features such as high thermal and oxidative stability, a relatively higher hydrophobicity and lipophobisity in combination with the electrical conductivity.

The synthesis of the head-to-tail 3,4'-bis(1,1-difluoroalkyl)-2,2'-bithiophene: model for the corresponding fluorinated polythiophene was accomplished. Unfortunately, this dimer was a liquid and we were not able to obtain its crystal structure. This was motivating for the preparation of the novel molecule: head-to-tail 3,4’,4’’-tri(difluoromethyl)-2,2’:5’,2’’-terthiophene which was crystallized and studied. This trimer has revealed an interesting inter- and intramolecular fluorine-sulfur interactions that shaped the molecule in the solid state. The sulfur-fluorine intermolecular distance is significantly shorter than the sum of the van der Waals radii. Based on the structural features and the face-to-face packing style, this molecule is an excellent model for an n-type oligomer or polymer. The two-dimensional face-to-face π-stacking motif is very advantageous to high charge mobility which makes the corresponding oligomer an ideal candidate for OFET (Organic Field Effect Transistors) devices.

Significant progress was made toward the synthesis of fluorinated fused five-membered ring systems. 1,3-dichloro-5,6-dihydrocyclopenta[*c*]thiophen-4-one is a key monomer was prepared using the literature method. The synthesis of 1,3-dichloro-4,4-difluoro-5,6-dihydrocyclopenta[*c*]thiophene which is a fluorinated thiophene monomer was accomplished. The synthesis of the head-to-tail (H-T) 3,3'-dichloro-4,4',5,5'-tetrahydro-1,1'-bi(cyclopenta[*c*]thiophene)-4,6'-dione and head-to-tail (H-H) 3,3'-dichloro-4,4',5,5'-tetrahydro-1,1'-bi(cyclopenta[*c*]thiophene)-6,6'-dione dimers were accomplished. Both dimers were obtained as a mixture of products and and we were not able to isolate the pure compounds. Crystals were obtained supposedly for the dimers were obtained. Unfortunately we were not able to resolve the x-ray crystal structures.

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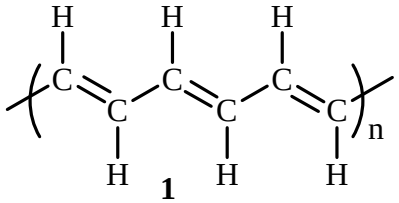
INTRODUCTION

1.1 Overview

1.1.1 Conducting polymers

The discovery that the extended π-electronic system of conjugated organic polymers provides properties which resemble those of the typical inorganic metals or semiconductors led to the emerging of a new field of chemistry.[1] These materials are different from most organic compounds which are traditional electric insulators. The highly conjugated chain with an extensive delocalization of π-electrons led to the electrical conductivity of the polymer upon doping (see section 1.1.2).



1

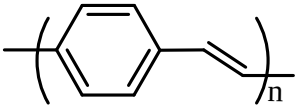
The synthesis of the *trans*-isomer of polyacytelene (**1**) as a new type of conducting material of conjugated organic polymer was reported in 1977 by Shirakawa, MacDiarmid, Heeger and co-workers. They reported that the conductivity of *trans*-polyacytelene (**1**) was increased by more than seven orders of magnitude when the polymer films were exposed to iodine vapor.[1,2] This fascinating discovery of conductive

polymers was recognized by the award of the chemistry Nobel prize in 2000 to Shirakawa, MacDiarmid and Heeger.

The major drawback of polyacetylene (**1**) is its instability in air and insolubility in organic solvents which renders the polymer unprocessable. In the following three decades after the discovery of the conducting polyacetylene (**1**), a large number of conjugated hydrocarbons, aromatic and aromatic heterocyclic conductive polymers such as poly(*p*-phenylene) (**2**)[3], poly(*p*-phenylenevinylene) (**3**)[4], polypyrrole (**4**)[5], polythiophene (**5**)[6], poly(alkylthiophene) (**6**)[7] and poly(3-alkoxythiophene) (**7**)[8], have been synthesized and extensively studied.

2

Poly(*p*-phenelene)



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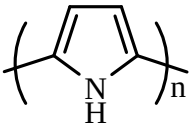
poly(*p*-phenylenevinylene)



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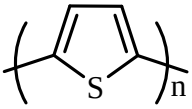
poly(pyrrole)



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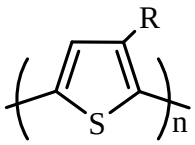
polythiophene



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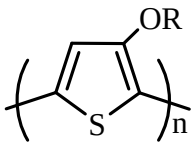
poly(3-alkylthiophene)



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poly(alkoxythiophene)

These materials have advantages over metals such as being lightweight due to low densities, processability and ease of fabrication, flexibility in design, mechanical strength, and resistance against chemical corrosion. Combining these properties with electrical properties and polymer processing makes conductive polymers ideal candidates for use in

the areas of optoelectronic devices such as organic light-emitting diodes[9] (OLED), field effect transistors[10] (FET), and chemical sensors.[11]

1.1.2 Electrical conductivity

The electrical conductivity σ (S/cm^{-1}) of a system is σ = nqμ where n is the total number of charge carriers, q is the charge on the charge carriers and μ is the mobility of the carrier.[12]

Organic conductive polymers are insulators or semiconductors in their neutral state because electrons can not move along the polymer backbones and throughout the material without the presence of charge carriers which are introduced through a process called doping. In this process the charge carriers are introduced typically via a series of oxidation or reduction reactions of the polymer. Semiconductors have conductivities of σ = 10^{-8} to 10^{-2} S/cm^{-1}, for example silicon has a conductivity σ = 10^{-5} S/cm^{-1}. Metals have conductivities of σ = 10^{-1} S/cm^{-1} and higher, for example copper has a conductivity σ = 10^{6} S/cm^{-1}.[13]

Table 1 Electrical conductivities of selected conductive polymers

Polymer	Maximum Conductivity S/cm^{-1}
Trans-polyacetylene (**1**)[14]	10^{5}
Poly(*p*-phenylene) (**2**)[3]	10^{4}
Poly(*p*-phenylenevinylene) (**3**) [15,16]	10^{4}
Polypyrrole (**4**)[5]	10^{2}-10^{3}
Polythiophene (**5**)[17]	10^{2}-10^{3}

Table 1 shows the values of the conductivities of selected doped conductive polymers. These values are dependent on the synthetic methods, dopant, regioregularity of the polymer and processing techniques.

1.1.3 Band gap

The electrical conductivity of a given material is dependent on the band structure, which is the energy gap (band gap) between the filled valence band (HOMO: highest occupied molecular orbital) and the unfilled conduction band (LUMO: lowest unoccupied molecular orbital) and the transport of electrons. The band gap is the energy required to promote valance band (HOMO) electrons into the conduction band (LUMO).

The interesting electronic properties of conductive polymers originate from the conjugated structure with alternating single and double bonds in the polymer backbone. In the ground state the alternating of shorter double bonds and longer single bonds opens an energy gap and transforms the polymer into a semiconductor. Experimentally the band gap is measured between the π-valance band (HOMO) and the π*-conduction band (LUMO).

Figure 1.1 shows the band structure of insulators, intrinsic semiconductors and metallic systems. In metallic systems there is an overlap between the valance band and the conduction band which allows the free flow of charge carriers between the two bands. In semiconductors the band gap is small and the number of charge carriers is low which renders the conductivity of these materials temperature dependent. At low temperatures the conductivity is very low and as the temperature increases the number of the exited charge carriers into the conduction band increases and so the conductivity increases.

Insulators have a very large band gap and they are incapable of moving charge carriers between the valance and the conduction band.

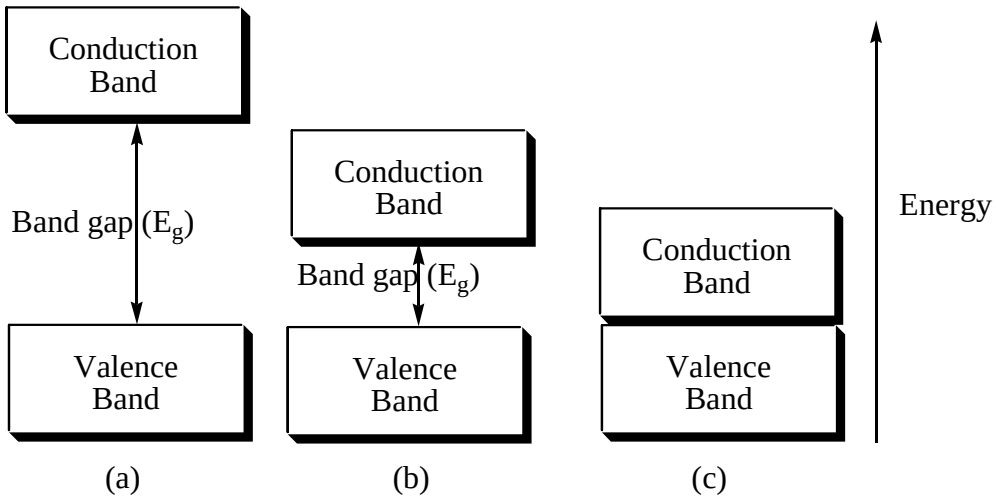


Figure 1 Band structure a) insulator b) semiconductor c) metallic system

Conductive polymers are considered insulators or sometimes semiconductors in their neutral state. The lack of charge carriers (electrons or holes) which are the prerequisite for electrical conductivity, limits the mobility of the electrons along the polymer backbones and through out the material. In the oxidative doping which corresponds to p-type doping, two new states are produced within the energy gap between the valence and the conduction bands, and the presence of these bands gives rise to new low-energy transitions in the doped material (Figure 1.2).[12,18] On the other hand, in the reductive doping which corresponds to n-type doping, electrons are injected into the conduction band and these electrons serve as the charge carriers.[19,20]

The oxidation of polythiophene (**5**) leads to the removal of electrons to produce conjugated radical cations (polarons) on the polymer chains as shown in Figure 1.3. The radical cations are delocalized over the polymer backbone. A dicationic bipolaron is

formed when a second oxidation occurs on the polymer chain. The removal of electrons results in a p-type doped polythiophene in which the positive charges (holes) are the majority of the mobile carriers for electrical conductivity.[21]

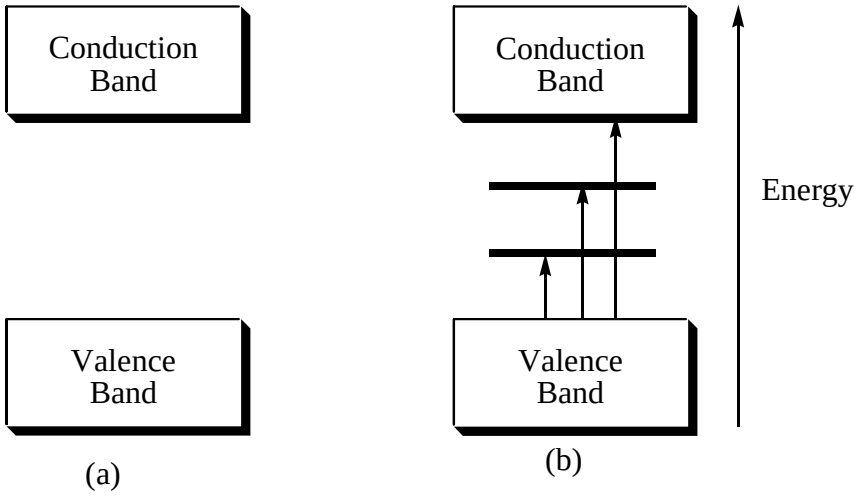


Figure 2 Transitions in a) an undoped and b) an oxidatively doped conductive polymer

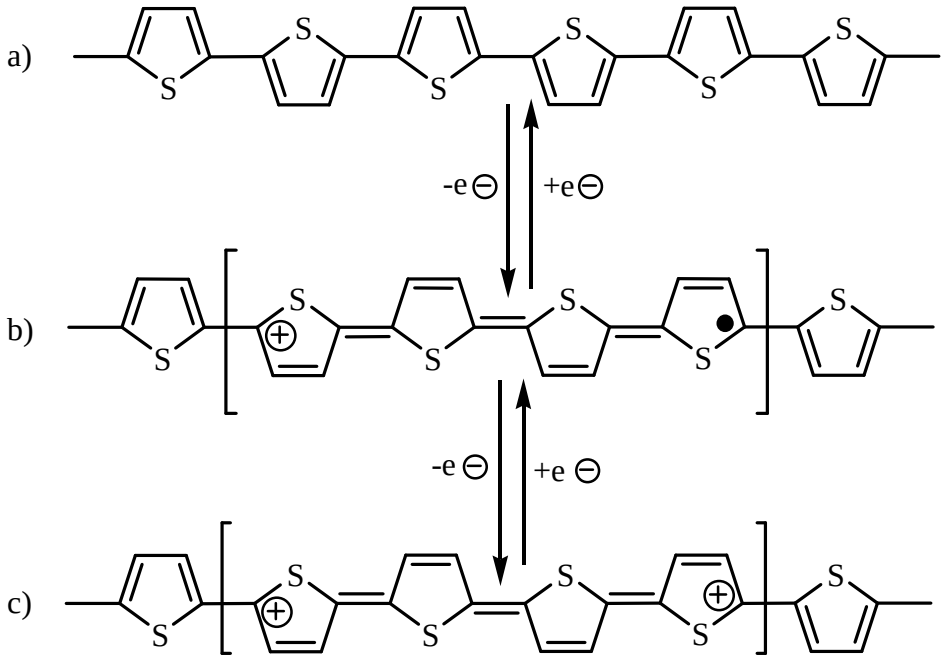


Figure 3 Oxidative doping charge carriers formation in polythiophene: a) neutral polymer b) polaron; and c) bipolaron.

The reduction of polythiophene (**5**) leads to the injection of electrons to produce conjugated radical anions (polarons) on the polymer chains Figure 1.4. The radical anions are delocalized over the polymer backbone. A dianionic bipolaron is formed when a second reduction occurs on the polymer chain. The injection of electrons results in an n-type doped polythiophene (**5**) in which the electrons are the majority of the mobile carriers for electrical conductivity.

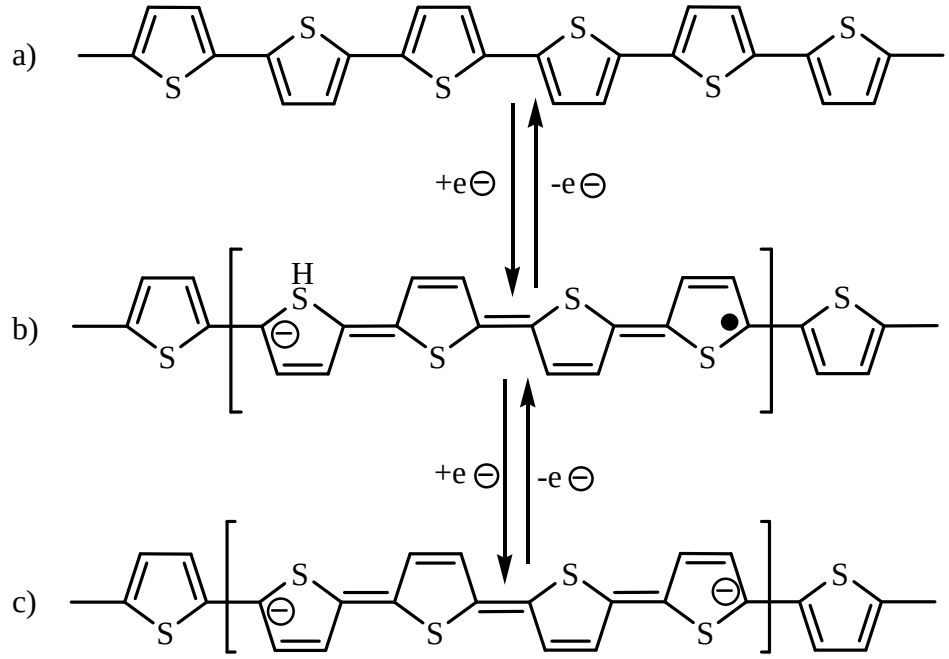


Figure 4 Reductive doping charge carriers formation in polythiophene: a) neutral polymer b) polaron; and c) bipolaron.

1.1.4 Low band gap conductive polymers

There is a strong interest in conjugated polymers with zero or very small band gaps, because they could be intrinsically conducting without the necessity of doping and,

in addition, in the doped state they are likely to be rendered optically transparent. The optical absorption is shifted to longer wavelength as the band gap gets smaller and when the absorption reaches the IR region the conductive polymer would become transparent. The optoelectronic properties of conductive polymers vary significantly with the band gap. The band gap of the conductive polymers depends on the degree of extended conjugation which relies heavily on the degree of planarity of the system. The planar systems lead to better overlap between orbitals which lead to a lowering of the band gap.

A general way to achieve low band gaps is to synthesize aromatic or heteroaromatic fused ring monomers and obtain the polymers from those monomers. Also by synthesis of regioregular structurally homogeneous polymers or by using polymers with fused ring systems which impart greater planarity to the system.[22-24]

Our ongoing research is focused on the synthesis of regioregular bithiophenes and studies of them as models for low band gap polythiophenes. In the following sections polythiophene and its derivatives that give a rise to low band gap materials will be discussed.

1.2 Polythiophenes

Thiophene is an aromatic heterocyclic molecule and one of the most studied heterocyles. The synthetic methodologies of thiophene and its applications have been widely studied over the last seven decades including thousands of publications about thiophene based compounds. The thiophene molecule has two different reactive sites: α and β to the sulfur atom which allows a wide variety of functionalization, and this aids in searching for molecules with desirable properties.[25]

In the past three decades polythiophenes, oligothiophenes and their substituted derivatives have been widely studied because of their electrical and electroluminescent (the generation of light by electrical excitation) properties. They have also received increasing attention because of their high chemical stability toward air and moisture, in both doped and undoped states, and ease of structural modification of the polymer backbone which leads to very good solubility of 3-substituted polythiohenes.[26,27]

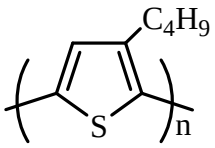
1.2.1 Substituted polythiophenes

Polythiophene is hard to process and is insoluble in most organic solvents, thereby presenting a significant obstacle for its characterization and possible industrial applications. Many studies were directed toward the development of a better conducting polymer with reasonably good solubility properties which are useful in the processing and characterization of the polymer.[28,29]

The first chemical synthesis of environmentally stable and soluble 3-substituted polythiophene was reported by Elsenbaumer and coworkers in 1985. They introduced a series of alkyl groups (methyl, ethyl, *n*-butyl) into the β-position of the thiophene ring. This was one of the most important discoveries regarding polythiophenes since it enhances the solubility and processibility of the polymer without appreciably altering its conductivity. In addition, the incorporation of the alkyl side chain into the 3-postion of polythiophene led to a full characterization of the polymer.

Poly(3-alkylthiophenes) bearing a relatively long-chain hydrocarbon substituent equal or greater than butyl like poly(3-*n*-butylthiophne) (**8**) showed improved solubility compared to the conductive forms of polythiophene (**5**) and poly(3-methylthiophene) (**9**)

which are not solution or melt processible. Poly(3-*n*-butylthiophne) (**8**) is soluble in many common organic solvents like toluene, tetrahydrofuran (THF), nitromethane, nitropropane and methylene chloride in its undoped form. The doped polymer is also soluble in common organic solvents like THF, nitromethane and dimethylformamide (DMF).[6,30]



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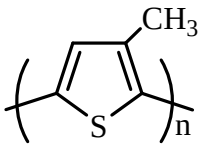
poly(3-*n*-butylthiophene)



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poly(3-methylthiophene)

The attachment of long-chain alkyl substituents into the thiophene ring improves the solubility and processibility of the polymer. However, steric interactions between the alkyl substituents and the polymer backbone tend to twist the thiophene ring and reduce the coplanarity of the polythiophene backbone, which decreases the degree of conjugation along the polymer chain and consequently increases the band gap.[31]

It is very important to find a balance between steric and electronic effects in designing systems that lead to lower band gaps like the synthesis of regioregular polythiophene which could minimize the steric effect.

1.2.2 Regioregular polythiophenes

The synthesis of poly(3-substituedthiophenes) by chemical oxidative polymerization or electrochemical polymerization methods led to various degrees of regioregularity since 3-substitutedthiophene is not a symmetrical molecule. In these cases the thiophene ring can react at either the 2- or the 5-postion. When two thiophenes are

coupled together, there are three available orientations which lead to the formation of three different dyads: head-to-tail (H-T) (2,5’ coupling), head-to-head (H-H) (2,2’ coupling) and tail-to-tail (T-T) (5,5’ coupling) and this leads to the formation of four isomeric triads in the polymer chain as illustrated in Figure 1.5.[27,32]

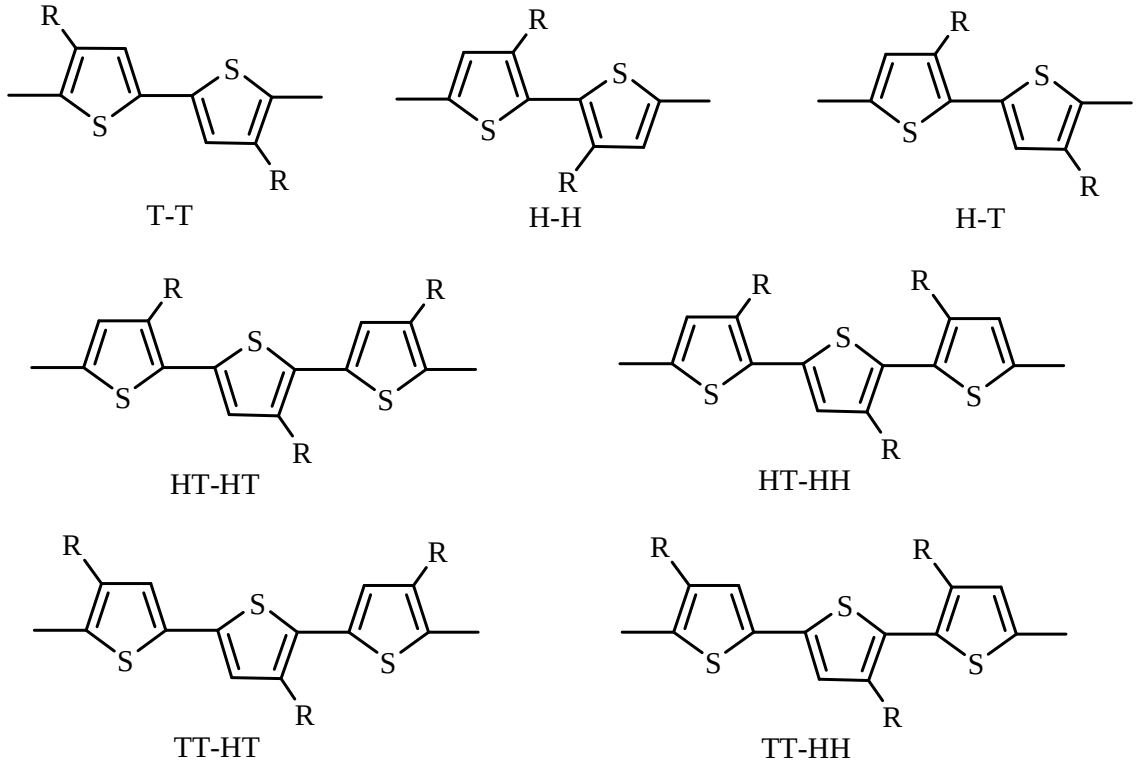


Figure 5 Illustration of the regioregular three dyads and four triads of 3-substituted polythiophene

The H-H isomer is unfavorable due to steric hindrance caused by encumbered H-H linkages which forces the torsional angles between the thiophene rings to twist out of the plane as shown in Figure 1.6. The twist from coplanarity lead to the loss of conjugation, higher band gap and reduction of electrical conductivity. It is extremely important to eliminate the presence of the H-H linkages when designing conductive

polymers. This could be achieved by the synthesis of H-T regioregular conductive polymers.

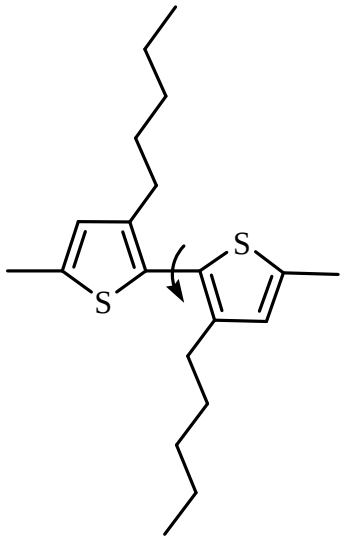


Figure 6 The H-H coupling twist thiophene rings out of planarity

1.2.3 Crystal structures of unsubstituted oligothiophenes

The structural calculations on short chain molecules (dimers, trimers, …, oligomers) as models for polythiophenes are a powerful strategy to investigate the conformational energies of the different regioisomers. The shortcomings of these calculations can not be ignored since the calculations were done on an optimized isolated molecule similar to a gaseous or dissolved molecule. It is highly desirable to obtain complete characterization of the oligothiophenes in the solid state. This gives a clear stereoview of the molecule and better understanding of the packing structure and the twist from planarity. The syntheses, characterizations and single crystal structure of several unsubstituted oligothiophenes as a model for polythiophene (**5**) have been reported in the literature.[33-35]

These studies showed that these unsubstituted oligomers exist in the all antiplanar (trans) conformations in which the sulfur atoms of the adjacent thiophene rings are anti to each other. Another interesting feature is the crystal packing in a herringbone structure (Figure 1.7)[36] common to all unsubstituted oligothiophenes which consist of strings of parallel molecules forming parallel layers on the top of each other.

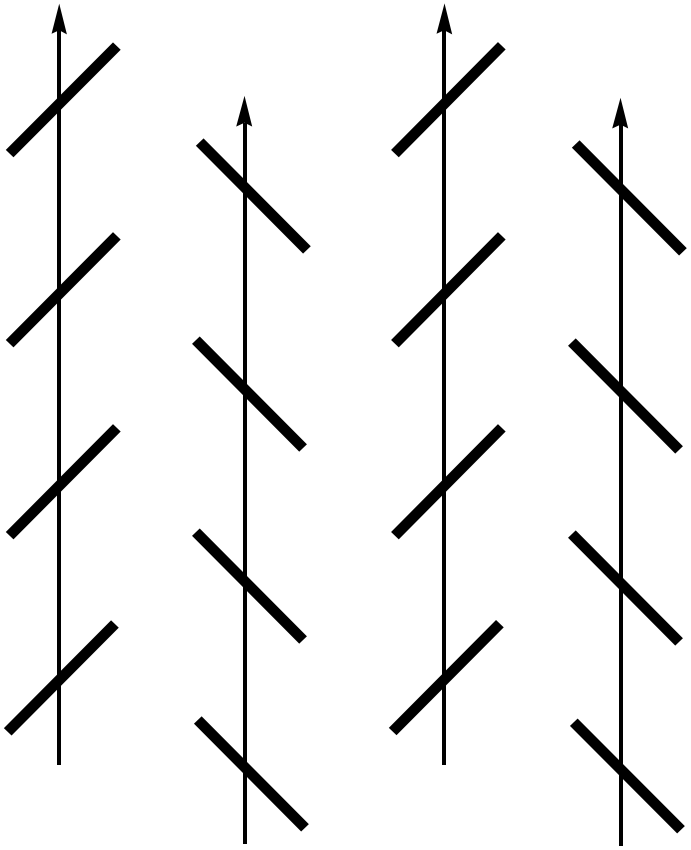
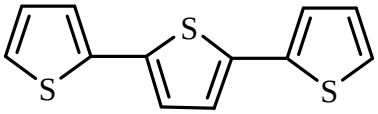


Figure 7 Representation of the herringbone structure

The single crystal x-ray data showed that all of these molecules are nearly planar with very low dihedral torsional angles. Also the crystal structure showed that these molecules pack in a herringbone structure. These results will be discussed in detail in the following section.

The x-ray crystal structure of α-terthiophene (**10**) (thiophene trimer) as a model for polythiophene (**5**) was reported.[37] The data showed that the adjacent thiophene rings are coplanar and the molecule is nearly but not completely planar. The molecule is slightly twisted from coplanarity and small torsional angles of 6-9° was observed. The x-ray crystal structure of α-quaterthiophene (**11**) (thiophene tetramer) was reported.[34,38] The data showed that the molecules pack in a herringbone structure and the molecule is planar with a very small (1.1°) dihedral angle. The crystal structure of α-sexithiophene (**12**) (thiophene hexamer) also was reported.[33,39] The results showed that **12** is completely planar with dihedral angles less than 1°. Interestingly, α-sexithiophene (**12**) is more planar than α-terthiophene (**10**). This could be due to the flexibility of the longer molecule which led to a better packing in the solid state. In addition, the α-sexithiophene (**12**) has six thiophene units which are more conjugated (longer conjugation) and are π-stacked better than four units of α-terthiophene (**10**).



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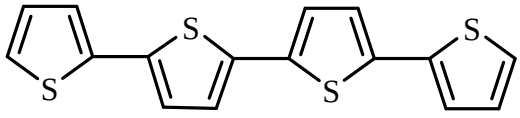

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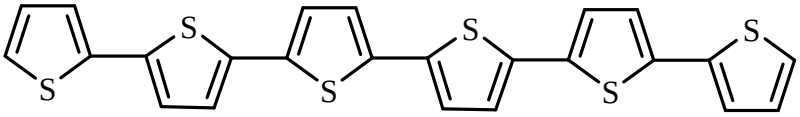

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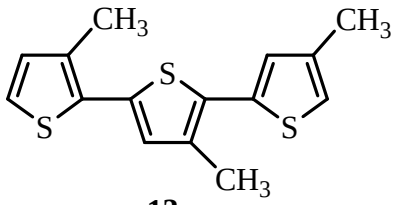
1.2.4 Crystal structures and calculations on substituted oligothiophenes

The introduction of alkyl substituents into the oligothiophene tends to twist the molecule from coplanarity. Several substituted oligothiophenes were synthesized and studied.[35,40,41] The synthesis, force field MM2 calculations and x-ray structure of 3,4',4''-trimethyl-2,2':5',2''-terthiophene (**13**), which is a 3-methylthiophene trimer with HT-HT couplings, was reported.[42]



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The x-ray structure analysis revealed that the trimer **13** is almost planar with small dihedral angles of 7.0 and 7.8° of the two outer thiophene rings with respect to the central thiophene ring. These results are similar to the x-ray structure of α-terthiophene (**10**) which has torsional angles of 6-9°. This could be explained as a result of the π-stacking which force the molecule to become planar in the solid state. Also the H-T linkages are favorable because they reduce the steric hindrance caused by the methyl substituents which enhances the planarity of the molecule. These observations could be confirmed also by looking at the UV-vis data in solution. The extent of conjugation of conjugated molecules is directly related to the π- π* transition, which appears as the maximum absorption of the material. The electronic spectra of conjugated molecules could provide a qualitative measurement of the π-orbital overlap which gives an insight to the extent of conjugation of the molecule. The λ_{max} of 3,4',4''-trimethyl-2,2':5',2''-terthiophene (**13**)

in chloroform was 20 nm less than that of the α-terthiophene (**10**) which suggests that the thiophene rings of **13** are more twisted in solution than that of **10**. The rotation barrier around the C-C bond that connects the two thiophene rings of **13** was 1.3 kcal mol^{-1} as calculated using force field MM2 calculations. This value is higher than that of **10** which is 0.6 kcal mol^{-1}. This also suggests that **13** is more twisted than **10**.[41,42]

McCullough performed molecular mechanics and ab initio (STO-3G level) calculations on 3-butylthiophene trimer (Figure 1.5, R = C_4H_9) with HT-HT and HT-HH couplings to examine the lowest energy conformation. The results showed that HT-HT coupling is 20° (molecular mechanics) and 25° (ab initio STO-3G level) twisted from coplanarity. The potential energy for twisting the ring from the coplanarity is less than 1 kcal based on both calculations. On the other hand, the introduction of the H-H coupling into the molecule severely twists the rings to an approximately 40° out of the coplanarity. Also the H-H structures are more than 5 kcal higher in energy than the H-T ones.[23]

1.2.5 Head-to-tail regioregular poly(3-alkylthiophene)

In recent years there has been a wide interest in studying regioregular substituted polythiophenes. In regioregular head-to-tail substituted poly(3-alkylthiophene) all units are attached head to tail, so that all the branches are lined up in one direction. Regioregular head-to-tail substituted poly(3-alkylthiophene) are known to have improved electrical conductivity and higher electroluminescence efficiency when compared with the corresponding regiorandom polymers. This has been attributed to the ability of thiophene rings to become coplanar and straighten polythiophenes into rods that can be π-stacked one layer on the top of the other. Also, the H-T couplings could adapt low energy

structures which enhance the coplanarity and lead to a greater π overlap along the polymer backbone which lead to a small band gap. One of the most important features of the regioregular H-T poly(3-alkylthiophenes) is the ability to self assemble into a highly ordered superamolecular structure. Poly(3-hexylthiophene) with 98% H-T coupling prepared by McCullough's group showed a well ordered structure with an interachian spacing of 16 Å and stacking distance of 3.8 Å between the polymer consecitive layers as shown in Figure 1.8. It is also showed a significant increase in electrical conductivity of the regioregular polymer over the regiorandom one.[23,43]

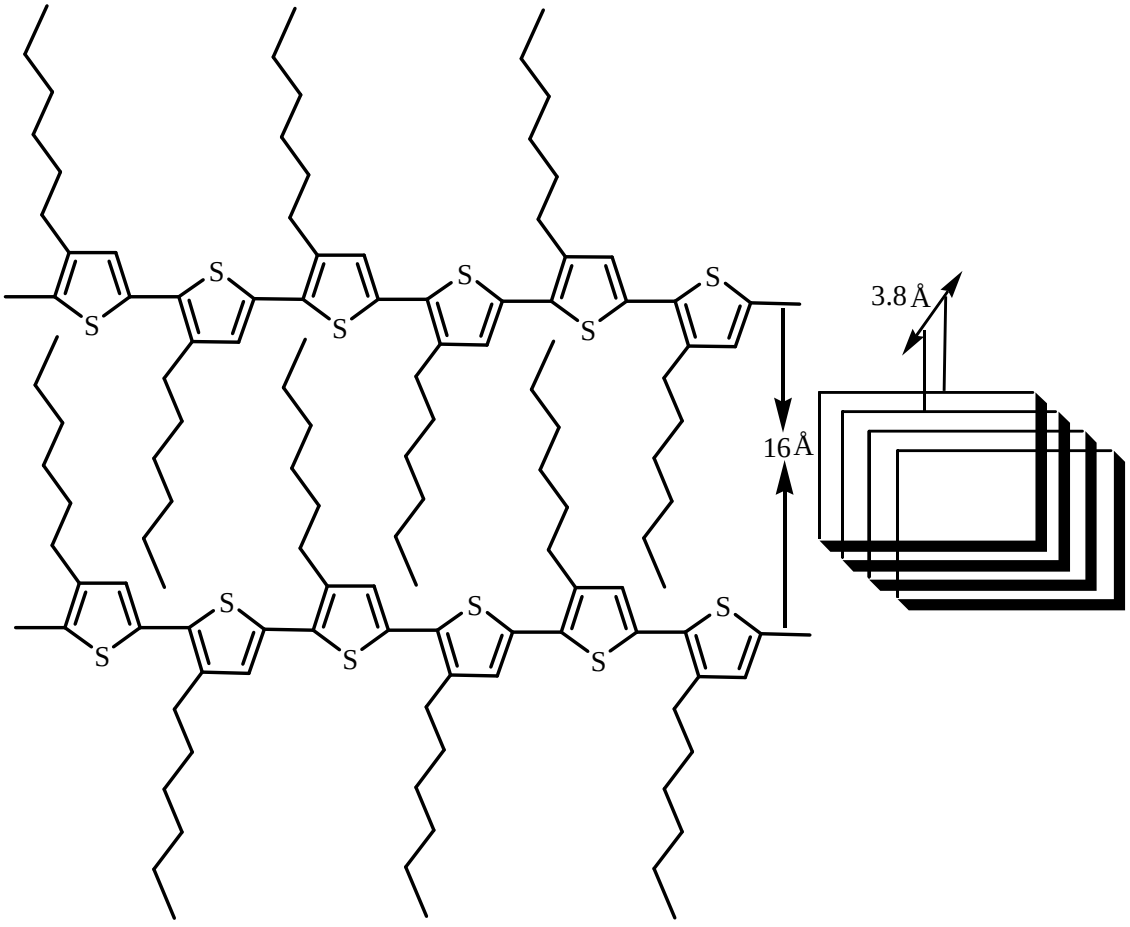
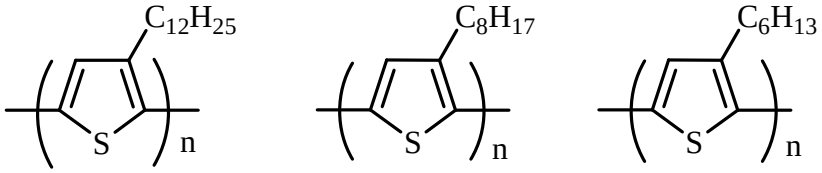


Figure 8 Regioregular H-T poly(3-alkylthiophene) self assembly in solid state

Regioregular H-T poly(3-alkylthiophene) showed improved electrical conductivities over the regiorandom polymers. The electrical conductivities and λ_{max} of the film of HT poly(3-alkylthiophene)s relative to the regiorandom poly(3-alkylthiophene)s is presented in Table 2. For example, iodine vapor doped cast films of H-T poly(3-dodecylthiophene) (**14**) shows a maximum electrical conductivity of 1000 S cm^{-1}. The regiorandom poly(3-dodecylthiophene) (**14**) shows a maximum electrical conductivity of 20 S cm^{-1} which is a significantly lower value than that of the H-T regioregular polymer. Also the λ_{max} "film" of the HT isomer is 562 nm which is shifted to lower energy relative to regiorandom isomer which exhibited a λ_{max} "film" of 480 nm.[43,44]



14 **15** **16**

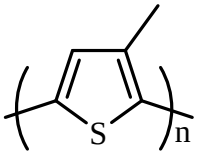
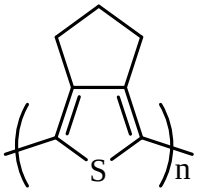
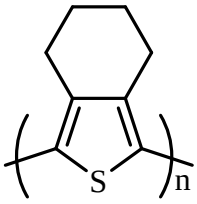
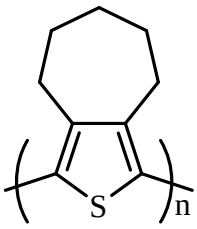
Table 2 Electrical conductivities and λ_{max} "film" of poly(3-alkylthiophene)s

Polymer	Maximum electrical conductivity	λ_{max} (nm) "film"
Poly(3-dodecylthiophene) (**14**) (HT)	1000 S cm^{-1}	562
Poly(3-dodecylthiophene) (**14**) (regiorandom)	20 S cm^{-1}	480
Poly(3-octylthiophene) (**15**) (HT)	200 S cm^{-1}	559
Poly(3-octylthiophene) (**15**) (regiorandom)	1 S cm^{-1}	480
Poly(3-hexylthiophene) (**16**) (HT)	100 S cm^{-1}	555
Poly(3-hexylthiophene) (**16**) (regiorandom)	1 S cm^{-1}	480

1.2.6 Fused ring systems

Another approach toward the reduction of the band gap is to minimize the steric effect and find a balance between the steric and electronic effects. This is accomplished by connecting the 3,4-substituents in a fused ring. Several poly(cyloalkyl[*c*]thiophene) with five, six and seven memberd fused rings have been synthesized and their optical spectral data shown in Table 3.

Table 3 polythiophenes and their maximum wavelength

Entry	Structure	λ_{max} /nm
1	 **9**	450
2	 **17**	610
3	 **18**	570
4	 **19**	460

The data shows that in the fused ring systems the optical spectra shifts to higher λ_{max} compared to poly(3-methylthiophene) (**9**). The results also showed that the optical spectra shifts to a shorter λ_{max} by increasing the ring size, five > six > seven-memberd ring.[45,46]

1.3 Fluorinated poly(thiophenes)

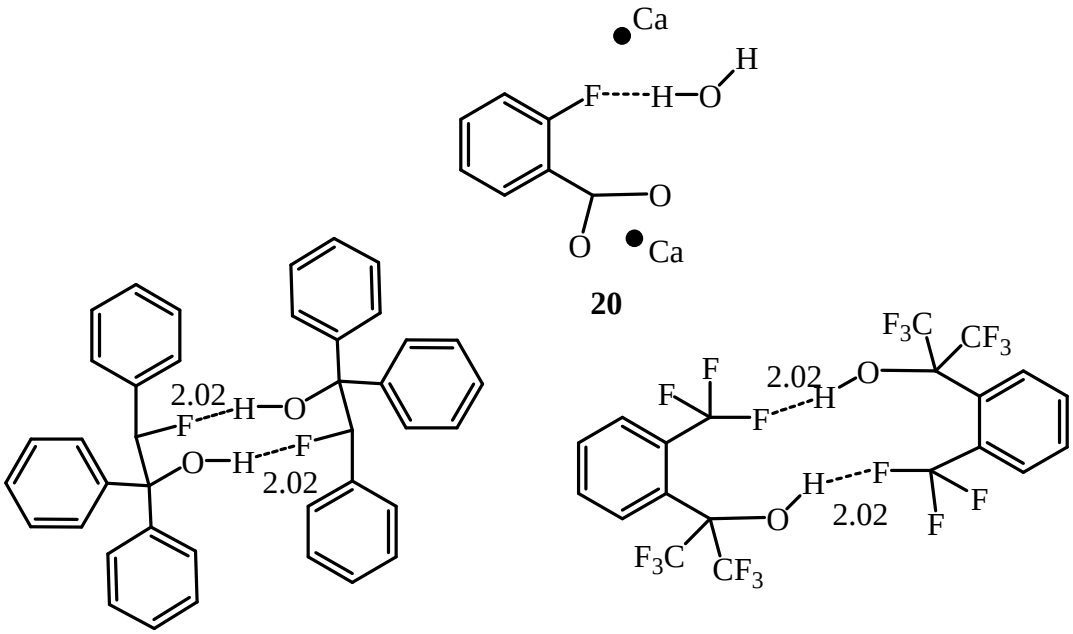
1.3.1 Fluoro-organic molecules

Fluorinated compounds have been used in a wide variety of applications that touches the daily life of millions of people around the globe. These uses include but not limited to, drinking water, dental products and pharmaceutical compounds. The physical and chemical properties of an organic molecule are changed substantially by the introduction of fluorine atoms to replace hydrogen atoms. Fluorine is the most electronegative atom among all known elements (on the Pauling scale EN = 4). Compared to other carbon-halogen bonds the C−F bond strength is the highest (460 kJ mol^{-1}). Fluorinated organic materials have remarkable features such as high thermal and oxidative stability, a relatively higher hydrophobicity and lipophobisity. [47,48]

1.3.2 "Organic fluorine hardly ever accepts hydrogen bonding" [49]

The influence of the fluorine-hydrogen interactions on the crystal structure was studied. Although fluorine atom is the most electronegative atom and it is expected to be a stronger hydrogen bonding accepter, the C-F group does not form a hydrogen bond. [50,51] This is supported by intensive search of Cambridge Crystallographic Structure Database (CSD) for crystal structures in which fluorine acts as a hydrogen bond acceptor. The search revealed that only 37 structures were possibly involved in fluorine-hydrogen

bonding and only two structures (**20**, **21**) showed O−H···F bonds. In calcium bis(2-fluorobenzoate) dihydrate (**20**) the fluorine atom has considerable anionic character since the water molecule is coordinated to Ca^{+2} which is more acidic than normal water. These are extraordinary conditions made the hydrogen bonding extremely favorable. 2-Fluoro-1,1,2-triphenylethanol (**21a**) has two O−H···F bonds. The molecule is packed into a dimer through an inversion center which led to the formation two O−H···F bonds.[49,52] A crystal structure of a compound **21b,** which is similar to **21a** also showed the same dimeric behavior in which two O−H···F bonds were formed.[53]



20

21a **21b**

Thalladi studied the C-H···F interactions in the crystal structure of fluorobenzene as shown in Figure 1.9. The previous studies suggests that weak C-H···F interactions do exist in these compounds but organic fluorine hardly ever accepts hydrogen bonds.

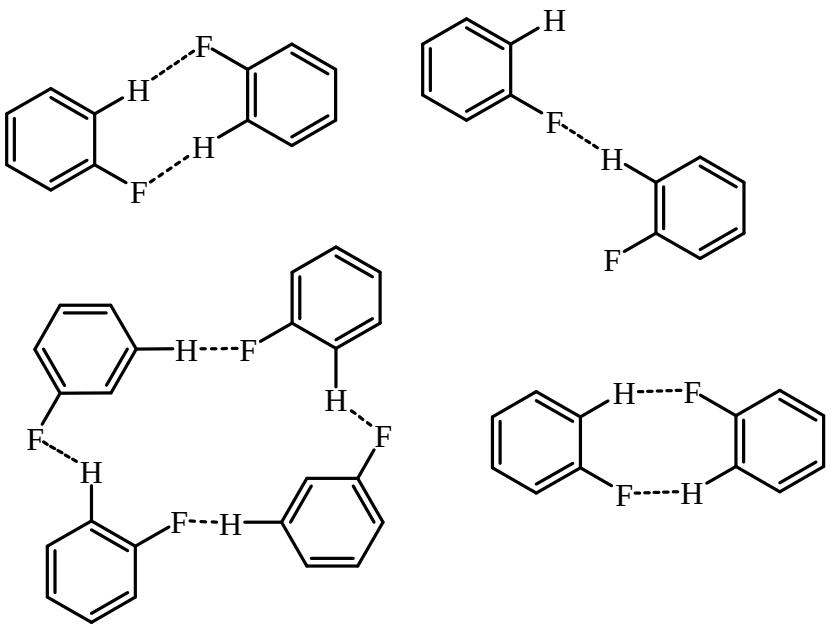


Figure 9 C-H···F Interactions in the crystal structure of fluorobenzene

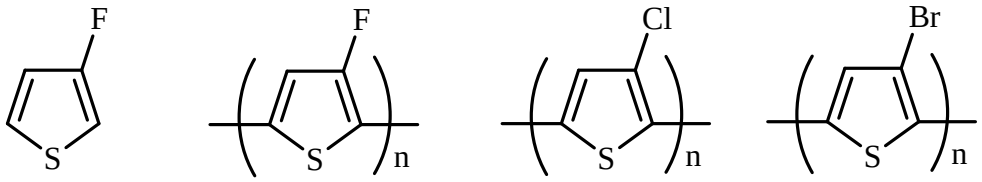
1.3.3 Fluorinated conductive polymers

There is a great interest in fluorinated conductive polymers due to the anticipated improvement in chemical and thermal stabilities relative to the alkyl analogues. Poly(thiophenes) are mainly p-type conductive polymers, therefore only positive charge carriers can be transported through the polymer backbone. On the other hand, fluorinated polythiophenes are under extensive investigations in the recent years because they are potential candidates for n-type semiconductors.[54-57]

1.3.4 Fluorinated polythiophenes

Fluorinated polythiophenes are very interesting materials. The association of the electrical conductivity of the polytiophene with the properties of the fluorinated organic molecules could lead to new polymers that possess much improved properties such as thermal stability, hydrophopicity and chemical inertness.

Lamaire and coworkers reported the synthesis and the electrochemical polymerization of 3-fluorothiophene (**22**). Poly(3-fluorothiophene) (**23**) exhibits improved properties and conductivity compared with poly(3-chlorothiophene) (**24**) and poly(3-bromothiophene) (**25**). This improvement could be attributed to the small size of the fluorine atom relative to the chlorine or the bromine atoms. The van der Waals radius of the fluorine atom is 1.47 Å compared to relatively high van der Waals radii values of 1.75 Å and 1.85 Å for the chlorine and the bromine atoms respectively. The big atomic size of the chlorine and bromine increases the steric hindrance which increases the dihedral angle between the thiophene rings and decreases the overlap between them resulting in the reduction of the conductivity as shown in Table 4.[58]



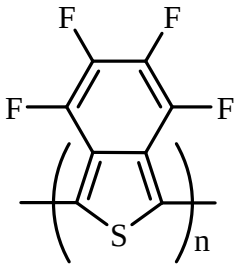
22 **23** **24** **25**

Table 4 Electrical conductivities of poly(halothiophenes)

Polymer	Conductivity S cm^{-1}
Poly(thiophene) (**5**)[17]	10^2-10^3
Poly(3-fluorothiophene)* (**23**)[58]	5
poly(3-chlorothiophene)* (**24**)[58]	$< 10^{-2}$
poly(3-bromothiophene)* (**25**)[58]	$< 10^{-2}$

* Regiorandom

The synthesis of poly(4,5,6,7-tetrafluoroisothianphthene) (**26**) was reported.[59] The motivation was to achieve a further reduction of the band gap and improvement in the solubility of the polymer compared to poly(isothianaphthene) (**27**). Polymer **26** is soluble in chlorinated and other organic solvents but in sharp contrast to poly(isothianaphthene) (**27**) which has a band gap value of 1 eV, the UV-vis spectrum of **26** shows a higher band gap value of 2.1 eV.[59] The higher band gap value could be due to the presence of F··· S interactions which twists the molecule.



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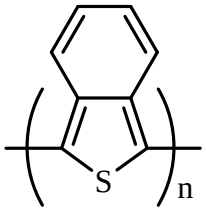

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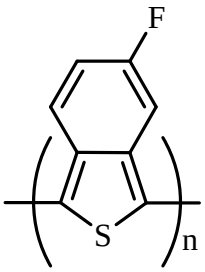

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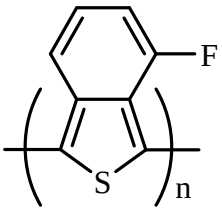

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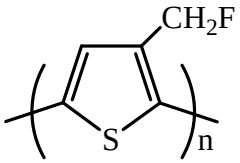
The substitution with a 5-fluoro moiety on the parent poly(isothianaphthene) (**27**) was also reported. Poly(5-fluoroisothianphthene) (**28**) has a reduced band gap value of 0.95 eV.[60] On the other hand, poly(4-fluoroisothianphthene) (**29**) was very difficult to n-dope with a negative onset potential of ca. -0.8 V compared to -0.6 V for **28**. It also shows a red color in the neutral state which resembles that of **26**. This suggests that **29** has a larger band gap even though both **28** and **29** have a single fluorine substituent. It is clear that the 4-substituent has a significant steric effect and causes an inter-ring twisting which led to an increase in the band gap.[61] It is also worth noting that the fluorine substituent(s) stabilized the n-doped form of the polymer. The peak potentials for the p-doping process of **28** and **29** (1.15 V) are slightly higher than that of **27** (1.04 V).

However, in contrast to the p-doping, the fluorine atom has a significant effect on the onset potentials of the n-doping. The onset potential for n-doping of **28** is 0.5 V more positive than that of **27**.[60-62]

The syntheses of polythiophenes with fluoroalkyl substituents have attracted a lot of research interest in the recent years. The fluorinated polymers are expected to possess improved chemical and thermal stabilities over the nonfluorinted polymers. The synthesis and study of three fluorinated 3-methylthiophene polymers **30**-**32** were reported.[63-65]



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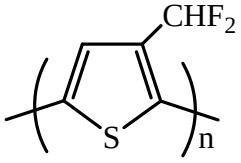

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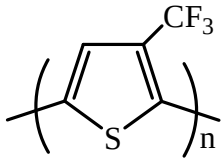

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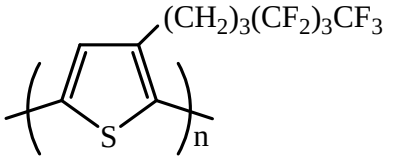
The oxidation potential of the poly(3-fluoromethylthiophene) (**30**) and poly(3-difluoromethylthiophene) (**31**) was high enough to oxidize a reduced poly(3-methylthiophene) (**9**) making these conductive polymers extremely attractive molecules as a cathode material in a cell which contains poly(3-methylthiophene) (**9**) as the anode. In comparison to poly(3-methylthiophene) (**9**) which showed a redox potential value of 0.96 V vs. Ag, **30** and **31** showed higher redox potential values of 1.33 and 1.4 V vs. Ag respectively. Although the oxidation potential increased as the number of fluorine atoms increased from **30** to **31**, it seems that poly(3-(trifluoromethyl)thiophene) (**32**) was observed to have a lower oxidation potential than **30** and **31**. The oxidized polymers are unstable when exposed to air and water, therefore the instability was reflected in the low conductivity (10^{-5} S cm^{-1}) of **30**.[63-65]

Poly[(1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluorononyl)thiophene] (**33**) exhibits an absorption maximum in the UV-vis spectrum at 488 nm in the solid state which is comparable to that of regiorandom poly(3-octylthiophene) (**15**). In addition, **33** exhibits a lower electrical conductivity (0.5 S cm^{-1}) compared to regiorandom poly(3-octylthiophene) (**15**). These results could be explained by the electron withdrawing effect of the fluorinated substituent and the lack of the regioregularity of the polymer backbone which give rise to the undesirable H-H linkages.



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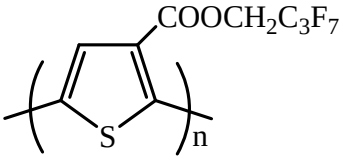

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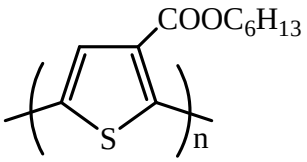

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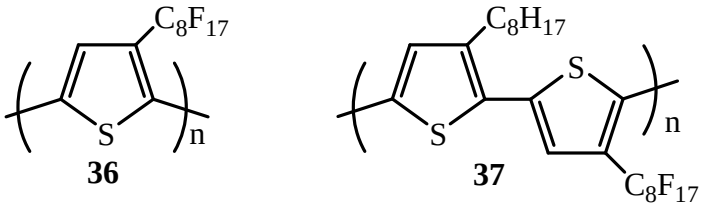
Polymer **34** was prepared and exhibited a bathochromic shift (410 to 370 nm) in the solid state compared to solution due to π-stacking in the solid state. This polymer exhibited a band gap of 2.4 eV.[66] Polymer **34** has a higher band gap compared to alkyl analogs such as poly(hexyl thiophene-3-carboxylate) (**35**) which exhibits an absorption maximum in the UV-vis spectrum at 408 and 436 nm in solution and film respectively.[67]

Collard and coworkers reported the synthesis and study of regiorandom polymers **36** and **37**. Poly(3-perfluorooctylthiophene) (**36**) showed a higher oxidation potential of 2.05 V compared to the oxidation potential of poy(3-octylthiophene) (**15**) which undergoes oxidation at 1.84 V. These results are consistent with the electron withdrawing effect of the perfluoroalkyl side chain. Poly(3-perfluorooctylthiophene) (**36**) was blue shifted by 114 nm from poly(3-octylthiophene) (**15**). This blue shift could be arised from the increasing number of H-H linkages and the bulkiness of the fluoroalkyl branch which

was high enough to twist the polymer backbone. In addition, the fluoroalkyl branch renders the polymer only soluble in supercritical carbon dioxide.[68]



36 **37**

In an attempt to overcome the twisting influence of the fluoroalkyl branch, Collard and coworkers synthesized **37** which is a copolymer of alternating 3-octylthiophene (**15**) and 3-(perfluorooctyl)thiophene units. The study showed (Table 5) that the oxidation potential of the copolymer **37** falls between the two homopolymer **15** and **36**.[68]

Table 5 UV-vis absorbtion and emission data

Polymer	Solution λ_{max} (nm)	Film λ_{max} (nm)	$\Delta \lambda_m$ (nm)	Band gap (eV)
15	441	515	74	1.83
37	384	456	72	2.07
36	326	338	12	2.52

The data in Table 5 showed that poly(3-perfluorooctylthiophene) (**36**) has a higher band gap value of 2.52 eV compared to alternating copolymer **37** which has a band gap value of 2.07 eV and poly(3-octylthiophene) (**15**) which has a band gap value of 1.83 eV. These results also showed that the alternating perfluoroalkyl-alkyl chain has overcome some of the twist caused by the bulky perfuoroalkyl chain especially in the

solid state. The $\Delta \lambda_m$ values which is the difference between λ_{max} solution and λ_{max} film, showed that in the twist caused by the perfuorinated chain was so severe and could not be overcome by the π-stacking in the solid state. However, in the alternating copolymer (**37**), the π-stacking effect in the solid state is significant since the λ_{max} film showed a red shift of 72 nm compared to λ_{max} solution.

1.4 Summary

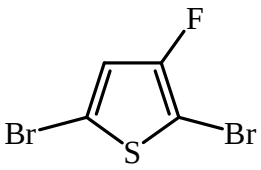
Based on the previous discussion, it is clear that fluorinated polythiophene systems are promising conducting polymers. It is well understood that manipulating the structure of monomers by the introduction of fluorine atom or fluorinated alkyl chain is of great importance to achieve high performance conducting materials and to fully comprehend the structure-property relationship of conjugated polymers.

As far as synthetic chemists are concerned, it is highly desirable to provide new efficient and convenient synthetic routes for the preparation of monomers that could be used as precursors for the synthesis of the polymeric material.

The synthetic organic chemistry of fluorinated thiophene derivatives provides a high level of structural flexibility, which allows the chemical, physical and electrical properties of the resultant polymers to be well tunable.

CHAPTER 2

SYNTHESIS AND CHARACTERIZATION OF 3-FLUOROTHIOPHENE (**18**) AND 2,5-DIBROMO-3-FLUOROTHIOPHENE (**38**) A PRECURSORS FOR CONDUCTIVE POLYMERS



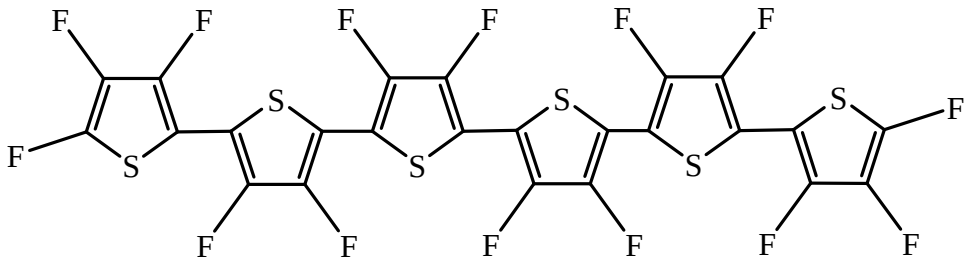
38

2.1 Overview

In the previous chapter the importance of fluorinated thiophenes as precursors for conductive polymers was discussed. One interesting aspect of perfluorination is the conversion of the conductive polymer from a p-type semiconductor to an n-type semiconductor. These materials that might be both reducible and oxidizable are potential candidates for FET applications. Perfluorinated oligo(*p*-phenylene)s were reported to be efficient n-type semiconductors.[69]

The synthesis, characterization and study of tetradecafluorosexithiophene (**39**) as an n-type semiconductor were reported. The absorption and emission spectra for this perfluorinated oligothiophene showed a blue shift relative to the non-fluorinated oligothiophene which results from the inductive effect of the fluorine atoms. The absorption and emission maxima of **39** are 421 and 471 nm, respectively, shifted to a

higher energy relative to 435 and 508 nm, the absorption and emission maxima of α-sexithiophene (**12**).[70] This result suggests a higher band gap for **39** relative to **12**. The X-ray crystallography of **39** revealed a planar structure with very small dihedral angle of 1.0°. Interestingly, DFT (density functional theory) calculations showed that the Mulliken atomic charges on internal fluorine which pointed toward the sulfur atom on the adjacent thiophene ring were more negative relative to the outer fluorine atoms and the internal sulfur atoms which pointed toward two fluorine atoms on the adjacent thiophene rings were more positive relative to the outer sulfur atom. These results strongly support the idea that in fluorinated thiophenes there is an attractive force that exists between the fluorine atom and the sulfur atom on the adjacent thiophene ring which might induce planarity of the polymer backbone.[70-72] The sulfur-fluorine distance is 2.918 Å which les than the sum (3.27 Å) of the van der Waals radii between the sulfur and the fluorine.



39

2.2 Syntheses of 3-fluorothiophene (**22**)

Our first approach toward preparation of fluorinated thiophenes is to synthesize 3-fluorothiophene (**18**) and 2,5-dibromo-3-fluorothiophene (**38**) as precursors for a wide variety of fluorinated conductive polymers. In contrast to **39** which has a locked structure

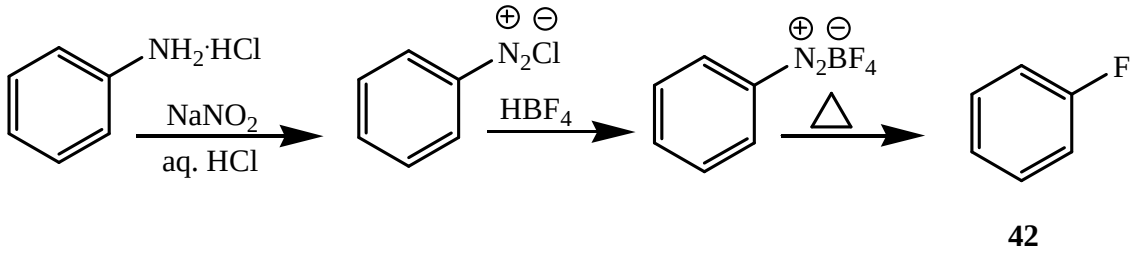
without the possibility of further functionalization, both 3-fluorothiophene (**22**) and 2,5-dibromo-3-fluorothiophene (**38**) have the 4-position of the thiophene ring available for further functionalization.

A review of the literature revealed that there are very few viable synthetic approaches that have been reported for the fluorination of the thiophene ring. These reports suffer from limitations such as low yield, lengthy precursor preparations and the use of expensive, hygroscopic or even dangerous materials as the fluorinating agent and this restricts their attractiveness for materials synthesis. In addition, many of these reports did not have sufficient experimental data and adequate characterization.

Our interest is to prepare fluorinated thiophene monomers that could be polymerized to produce conductive polymers. For this purpose the 2- and the 5-positions should be available for the polymerization reaction to take place. 3-Fluorothiophene (**22**) and 2,5-dibromo-3-fluorothiophene (**38**) are strong candidates for such polymers. They also could be used in a wide variety and diverse applications.[73]

Although 3-fluorothiophene (**22**) is a small and simple molecule it's synthesis is challenging and far from being straightforward. The thiophene ring is highly reactive at the 2- position relative to the 3-position. The earlier reports on the attempted synthesis of 3-fluorothiophene (**22**) proved to be unsuccessful; they include the reaction of antimony trifluoride with either 3-bromothiophene (**40**) or 3-chlorothiophene (**41**) and the reaction of aluminum trifluoride with 3-chlorothiophene (**41**).[74] The early report on the attempted introduction of the fluorine into the thiophene ring using the Schiemann reaction, in which the fluoroaromatic compound is generated from the thermal decomposition of the

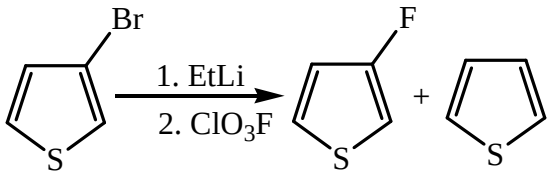
aryl diazonium tetrafluoroborate,[75] was unsuccessful. Flood's synthesis of fluorobenzene (**42**) from benzene diazonium tetrafluoroborate is shown in Scheme 1.[76] An unsuccessful attempt was made to adapt the same synthetic methodology, in which the fluoroboric acid was reacted with thiophene diazonium chloride ,to prepare fluorinated thiophenes.[77]



42

Scheme 1 Flood's synthesis of fluorobenzene (**42**)

Sharma and coworkers[78] were the first to report the synthesis and characterization of 3-fluorothiophene (**22**) by halogen metal exchange between 3-bromothiophene (**40**) and ethyllithium at -50 ºC followed by reaction with perchloryl fluoride as shown in Scheme 2.



40 **22** **43**

Scheme 2 Synthesis of 3-fluorothiophene (**22**) by Gronowitz method

The authors[78] pointed out that 3-fluorothiophene (**22**) could be separated from thiophene (**43**) (the byproduct of the reaction) by means of preparative gas chromatography. The product was a mixture consisting of 3-fluorothiophene (**22**) and thiophene in a 77% to 23% ratio, based on the preparative gas chromatography, but the

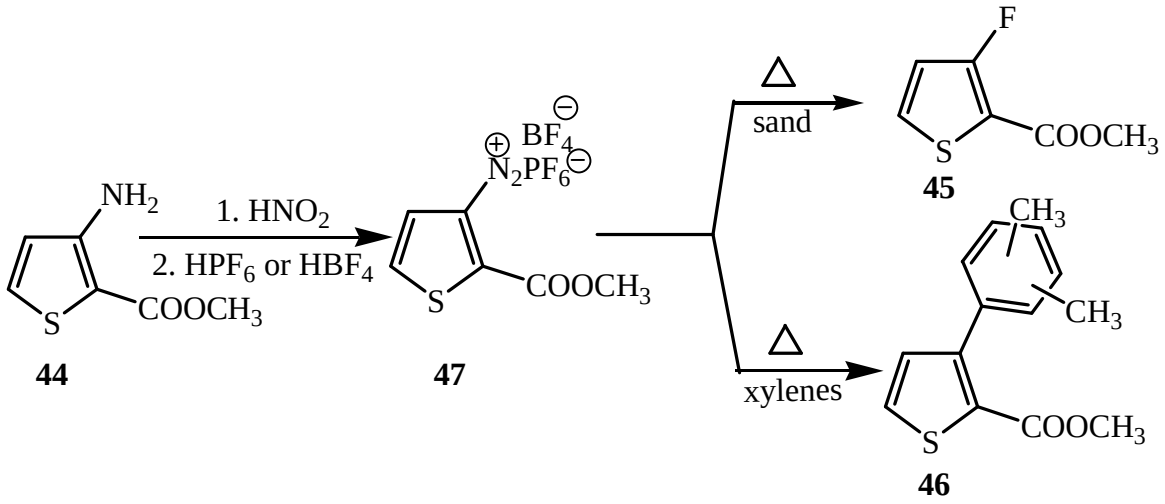
percentage yield of the isolated product was not reported. The product **22** was characterized by ^{1}H NMR and ^{19}F NMR spectroscopy.[78] In this method the use of perchloryl fluoride as the fluorinating agent, which is dangerous to handle,[79-81] made the use of this synthetic approach inconvenient for preparative scale reactions.

Corral[82] was the "first" to report the introduction of the fluorine atom into the thiophene ring using the Schiemann reaction, in which the author claimed that diazotization of methyl 3-aminothiophene-2-carboxylate (**44**) followed by the addition of tetrafluoroboric acid or hexafluorophosphoric acid and then thermal decomposition in boiling xylene gave methyl 3-fluorothiophene-2-carboxylate (**45**) in 48 and 92% yield respectively, as a normal Schiemann reaction.

Kobarfard[83] reported that conducting the Schiemann reaction on methyl 3-aminothiophene-2-carboxylate (**44**) exactly as described by Corral[82] led to a product with a similar melting point (112 ºC) to the one that was reported by Corral[82] but with an extra two ^{1}H NMR spectral peaks. Also, the mass spectrum showed a molecular ion at mass of 246. These data, accompanied by elemental analysis, revealed that the product of this reaction was a methyl 3-(dimethylphenyl)thiophene-2-carboxylate (**46**). In fact methyl 3-(dimethylphenyl)thiophene-2-carboxylate (**46**) is the product of Gomberg reaction (the coupling of the aromatic part of the diazonium salt with another aromatic ring),[84] between the diazonium salt **47** and xylenes as shown in Scheme 3.

Kobarfard[83] reported the first successful Schiemann reaction on any type of thiophene ring as shown in Scheme 3. They obtained methyl 3-fluorothiophene-2-carboxylate (**45**) in 30% yield by heating the mixture of diazonium salt **47** and sand under

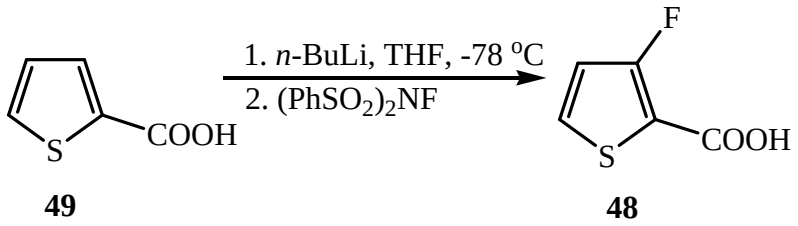
vacuum (0.1-1 torr). Their ^{1}H NMR and ^{19}F NMR spectra, and elemental analysis supported the structure of methyl 3-fluorothiophene-2-carboxylate (**45**) which was obtained as a solid material that had a melting point of 51-53 ºC.



Scheme 3 Synthesis of methyl 3-fluorothiophene-2-carboxylate (**45**) by Schiemann reaction

Sampson[85] reported the synthesis of methyl 3-fluorothiophene-2-carboxylate (**45**) in 47% yield by heating the mixture of diazonium salt **47** and sand under vacuum (0.1-1 torr) at ca. 200 ºC and trapping the reaction product using a cold finger.

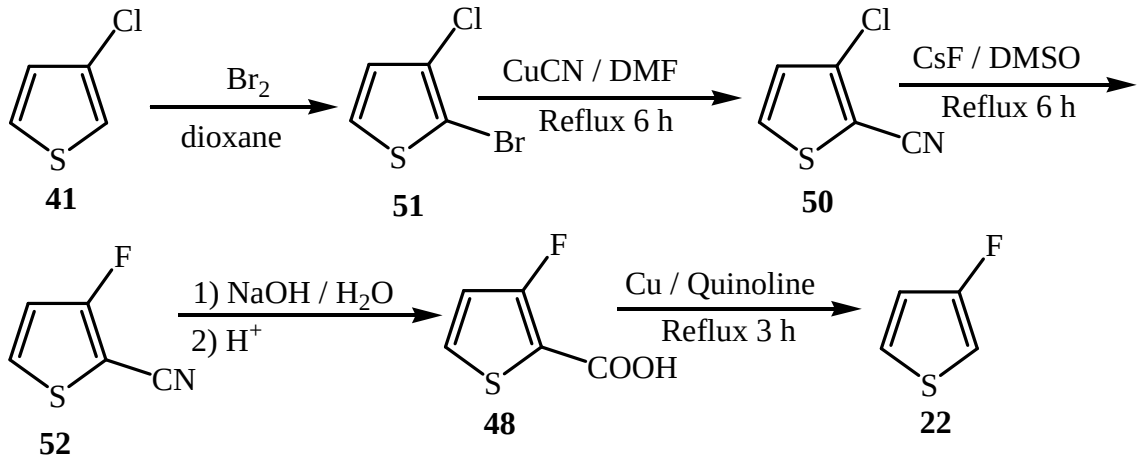
The synthesis of 3-fluorothiophene-2-carboxylicacid (**48**) from thiophene-2-carboxylic acid (**49**) using n-butyllithium and N-fluorobenzenesulfonimide as shown in Scheme 4 has also been reported.[86,87] Although it is a one step synthesis, the use of the expensive and highly hygroscopic N-fluorobenzenesulfonimide as the fluorinating agent restricts the attractiveness of this method for the synthesis of fluorinated thiophenes.



49 **48**

Scheme 4 Synthesis of 3-fluorothiophene-2-carboxylic acid (**48**)

Lemaire[88] also reported the synthesis of 3-fluorothiophene (**22**) by cesium fluoride mediated fluorination of 3-chloro-2-cyanothiophene (**50**), Scheme 5.



41 **51** **50** **52** **48** **22**

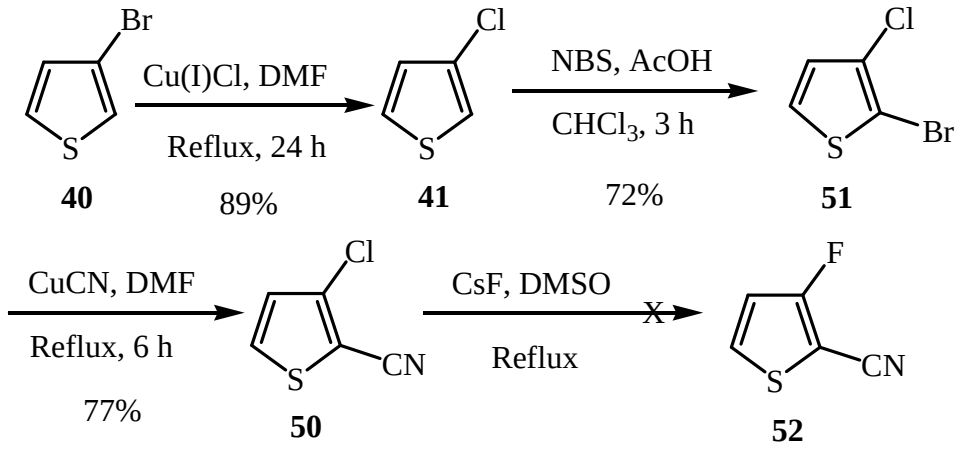
Scheme 5 Synthesis of 3-fluorothiophene (22) by Lemaire

In this method 3-chlorothiophene (**41**) was brominated at the 2-position to generate 2-bromo-3-chlorothiophene (**51**), then the cyano group was selectively introduced at the 2-position. The fluorine atom was introduced into the thiophene ring by treating 3-chloro-2-cyanothiophene (**50**) with an excess of cesium fluoride to produce 2-cyano-3-fluorothiophene (**52**) which was hydrolyzed and decarboxylated to afford 3-fluorothiophene (**22**).

The drawback of this method of the synthesis of 3-fluorothiophene (**18**) is the use of a lengthy synthetic preparation approach, very low yield (8.3% overall) and the purification problems the author encountered during the critical synthetic step of 2-cyano-3-fluorothiophene (**49**) preparation.

2.3 Synthesis of 3-fluorothiophene (**22**)

We used Lemaire's procedure for the preparation of 2-cyano-3-fluorothiophene (**52**), in an attempt to synthesize 3-fluorothiophene (**22**) as shown in Scheme 6.



40 **41** **51** **50** **52**

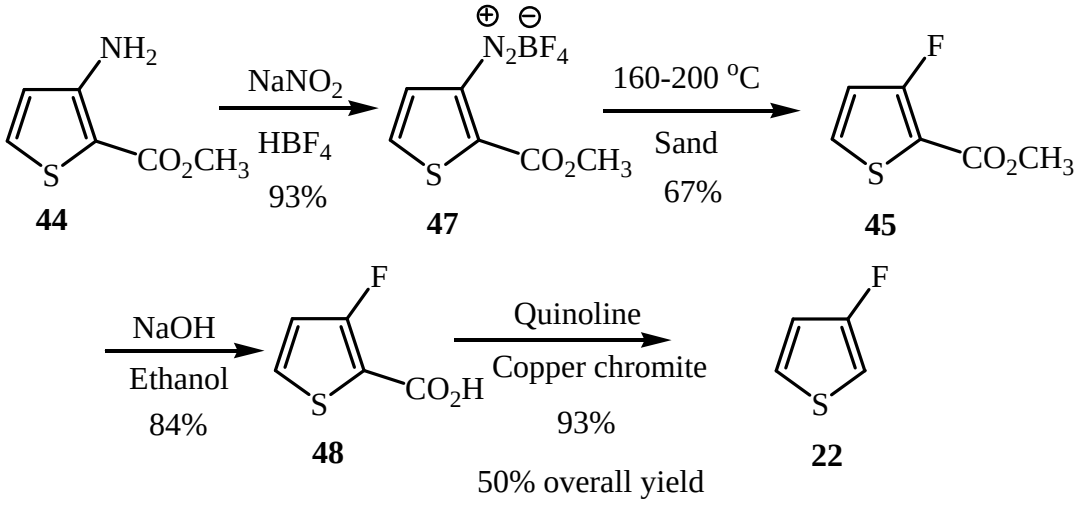
Scheme 6 An attempted synthesis of 2-cyano-3-fluorothiophene (**52**)

3-Chlorothiophene (**41**) was prepared via a halogen exchange reaction by reacting 3-bomothiophene (**40**) with copper(I) chloride.[89] 3-Chlorothiophene (**41**) codistilled with water and was collected via Dean-Stark trap. It was obtained in 89% yield by distilling the crude product under vacuum. **41** was brominated with NBS (N-bromosuccinimide) selectively at the 2-position to yield 2-bromo-3-chlorothiophene (**51**) in 72% yield.[90] 3-Chloro-2-cyanothiophene (**50**) was prepared in 77% yield by the literature method using

copper(I) cyanide for the selective exchange of the bromine with the cyano group at the 2-position.

Attempts to introduce a fluorine atom into the thiophene ring through a halogen exchange reaction of 3-chloro-2-cyanothiophene (**50**) with CsF turned out to be very problematic. The reaction was conducted repeatedly as described by Lemaire.[88] Our ^{1}H NMR spectrum and TLC, however, showed a mixture of many substituted thiophenes, but ^{19}F NMR spectroscopy showed two doublets at -119.01 ppm (d, J = 4.6 Hz) and -119.03 (d, J = 4.6 Hz). The separation of these compounds and the identification of the molecule giving rise to this ^{19}F NMR spectrum was not possible.

Our second approach toward the attempted synthesis of 3-fluorothiophene (**22**) was to use the special conditions for the Schiemann reaction as reported by Kobarfard[83] and Sampson as shown in Scheme 7.[85]



Scheme 7 Synthesis of 3-fluorothiophene (**22**)

The key intermediate for the synthesis of methyl 3-fluorothiophene-2-carboxylate (**45**), methyl 3-aminothiophene-2-carboxylate (**44**) was diazotized with sodium nitrite followed by the addition of tetrafluoroboric acid which gave the corresponding diazonium salt **47** in quantitative yield. A mixture of 2-methoxycarbonylthiophene-3-diazonium tetrafluoroborate (**47**) and sand was heated under vacuum (0.1 Torr) at ca. 180 ºC. When the oil-bath temperature reached 160 ºC a crystalline product started to sublime and was trapped with a liquid nitrogen cold finger. Also, a pale yellow liquid was distilled and solidified inside the distillation apparatus. The solid and the solidified liquid were combined and dissolved in methanol to yield methyl 3-fluorothiophene-2-carboxylate (**45**) in a good yield of 67% after precipitation by the addition of water to the solution. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectroscopy and elemental analysis supported the structure of the product, methyl 3-fluorothiophene-2-carboxylate (**45**).[73]

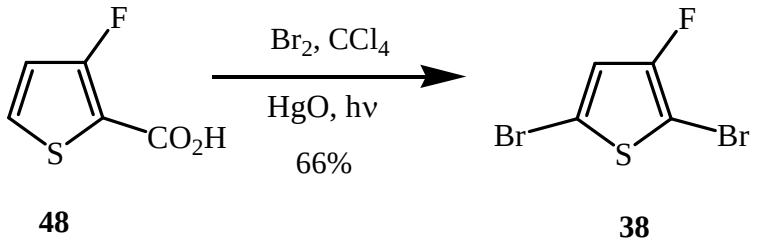
3-Fluorothiophene-2-carboxylic acid (**48**) was obtained in 84% by the hydrolysis of **45** using sodium hydroxide. The decarboxylation of **48** was carried out similar to a reported substituted thiophene-2-carbxylic acid decarboxylation[91] using barium promoted copper chromite in quinoline. 3-Fluorothiophene (**22**) was obtained in 93% yield by direct distillation from the reaction mixture. The purity of **22** was greater than approximately 97% as shown by the ^{1}H NMR spectrum. The overall yield from **44** to **22** was 49%.

2.4 Synthesis of 2,5-dibromo-3-fluorothiophene (**38**)

Our next target was the preparation of 2,5-dibromo-3-fluorothiophene (**38**) as a precursor for conductive polymers. Gronowitz[92] previously reported the synthesis of **38**

by bromination of 3-fluorothiophene (**22**). The product was obtained as a mixture of **38** and 2,3-dibromothiophene.

2,5-Dibromo-3-fluorothiophene (**34**) was synthesized using a photoassisted Cristol-Firth-Hunsdiecker reaction as shown in Scheme 8.[93] 3-Fluorothiophene-2-carboxylic acid (**48**) was brominated with 2 equivalents of bromine and the reaction was irradiated with 150-W bulb in the presence of red mercuric oxide. The product **38** was obtained in 66% yield.



48 **38**

Scheme 8 Synthesis of 2,5-Dibromo-3-fluorothiophene (**38**)

2.5 Conclusion

The synthesis of 3-fluorothiophene (**22**) was accomplished by a very convenient method, which led to a relatively high yield and pure compound. No expensive fluorinating agents were used. 2,5-Dibromo-3-fluorothiophene (**38**), a potential monomer for a variety of fluorinated bithiophenes and polythiophenes has been synthesized.

CHAPTER 3

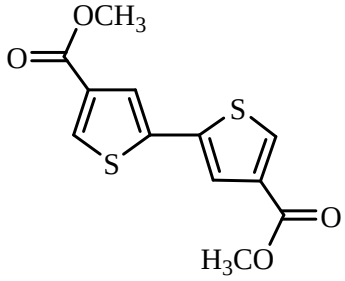
SYNTHESIS AND STUDY OF FLUOROALKYL THIOPHENES, BITHIOPHENES AND TRITHIOPHENES: MODELS FOR THE POLYMERIC MATERIAL

3.1 Bithiophenes: the model study

In the recent years, the investigations done our group have been focused on the synthesis of planar regioregular bithiophenes and studies of them as models for polythiophenes. The model studies showed that head-to-head (H-H) linkages render the dimers highly twisted and consequently reduces the electrical conductivity of the corresponding polymer. The twist around the thiphene-thiophene single bond led to a considerably high rotation barrier which reduces the conjugation along the polymer backbone.

Pomerantz[94,95] has employed ab initio calculations [3-21G*] to examine the dihedral angles and the rotation barriers around the thiophene-thiophene single bond of the dimethyl 2,2'-bithiophene 4,4'-dicarboxylate (**53**) [tail-to-tail (T-T)], dimethyl 2,2'-bithiophene 3,4'-dicarboxylate (**54**) [head-to-tail (H-T)], dimethyl 2,2'-bithiophene 3,3'-dicarboxylate (**55**) [head-to-head (H-H)] and dipropylbithiophenes **56**-**58**. The study showed that the T-T isomers **53** and **56** essentially had typical coplanar thiophene rings and the sulfur atoms exist in transoid conformation. The calculated dihedral angle values for **53** and **56** were 35° and 32.6° and the rotation barriers values were 0.37 and 0.34

kcal/mol. For both H-H isomers **52** and **55** the calculated dihedral angle and the rotation barrier values were also unexceptional. They both showed a relatively high dihedral angle (**55**: 56.8°, **58**: 86.6°) and high rotational barrier (**55**: 8.55, **58**: 7.84 kcal/mol) due to the steric hindrance caused by the bulky groups. The calculations showed that H-T isomer **54** was special when compared to **57**. Interestingly, the dihedral angle (**54**: 21.7° and 17.4°, **57**: 58.7°) and the rotation barrier (**54**: 0.084, **57**:2.27 kcal/mole) values were significantly low regardless of the fact that a bigger ester group has replaced a smaller hydrogen atom.



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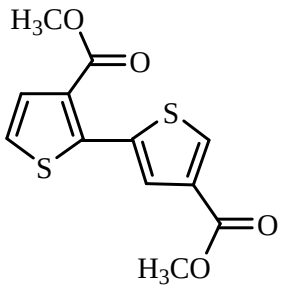

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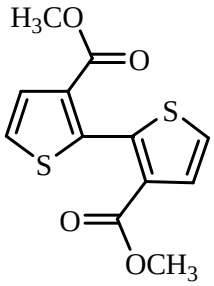

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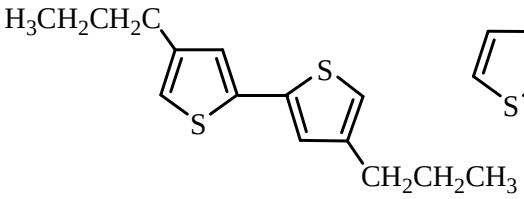

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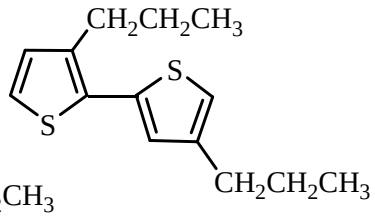

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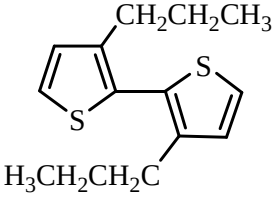


58

The study showed that the structure was stabilized by intramolecular attractive interactions that exist between the negative carbonyl oxygen and the positive sulfur atom in the adjacent thiophene ring which led to reduced dihedral angle and rotational barrier. In these systems the distance between the oxygen and the sulfur is significantly smaller

than the sum of the oxygen and sulfur van der Waals radii. The distance between the oxygen atom and the sulfur atoms is 2.668 Å is considerably smaller than 3.22 Å, which is the sum of van der Waals radii of the two atoms.[94,95] These sulfur-oxygen interactions renders the dimer, and consequently the corresponding polymer, planar which has strong implications on the ease of the charge transport through the polymer.

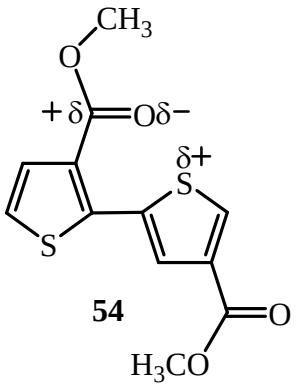
The synthesis of these molecules and the X-ray crystal structures provided a powerful tool that demonstrate the existence of these attractive interactions and gave an insight view of these molecules in the solid state. Pomerantz reported the synthesis and study of the three bithiophene ester isomers **53-55**. The X-ray crystal structure revealed that structures **53** and **54** are planar, or very close to planar, in the solid state. The dihedral angle of the T-T isomer **53** in the solid state was 0.4°, whereas the calculated dihedral angle was 35.1° which was considerably different from the observed value. This could be explained by the low rotation barrier that allows the rings to become coplanar due to the packing forces in the solid state. The low rotation barrier allows the π-stacking to overcome the steric effect in the solid state.

The H-T isomer **54** was also observed to be nearly flat with coplanar thiophene rings. The observed dihedral angle values of 2.7° and 3.8° are significantly less than the calculated values of 21.7° and 17.4° respectively. The observed value (2.668Å) of the distance between the carbonyl oxygen and the sulfur of the distal ring mirrors the calculated results (2.662Å) which is considerably shorter than the sum of the van der Waals radii (3.32Å) of the sulfur and oxygen. These results confirm the presence of an electrostatic attraction between the carbonyl oxygen and the sulfur of the distal thiophene

ring. The electrostatic attraction between the carbonyl oxygen and the sulfur of the distal thiophene ring, the low rotational barrier and the packing forces induced the planarity of the molecule in the solid state. The X-ray structure of the corresponding H-H isomer **55** showed a very twisted 74.8° dihedral angle, while the calculated value was 56.8° and in both cases the stable conformation was with the sulfur atoms syn.[95,96] The presence of the H-H linkages must be eliminated since they tend to severely twist the molecule which is disadvantageous to the charge mobility. Our model study was mainly limited to the synthesis of molecules with H-T linkages.

3.2 Fluorinated bithiophenes: the model study

Based on the previous discussion we envisioned that the head-to-tail 3,4'-bis(1,1-difluoroheptyl)-2,2'-bithiophenes (**59**) could exhibit a similar behavior to **54**.



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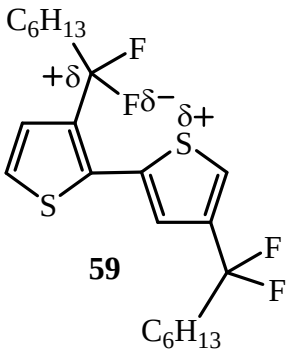

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Fluorine is the most electronegative atom among all elements and it is expected to attract the electropositive sulfur atom on the adjacent thiophene ring. These attractive forces are extremely significant to render the dimer planar or to cause a significant reduction in the dihedral angle. In addition, the presence of the fluorine in the molecule might alter the crystal packing of the molecule in the solid state as a result of the inter-

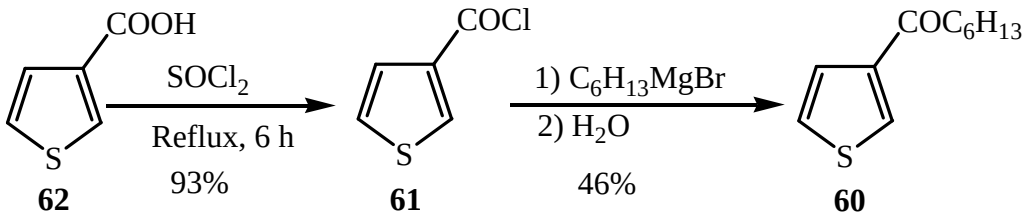
and intramolecular interactions. The exploration of these interesting features led to the synthesis and study of the H-T 3,4'-bis(1,1-difluoroheptyl)-2,2'-bithiophenes (**59**).

3.3 Syntheses of 3-heptanoylthiophene (**60**)

*3.3.1 Synthesis of 3-heptanoylthiophene (**60**) by the Grignard reaction*

3-Heptanoylthiophene (**60**) is the key intermediate in the synthetic route toward the preparation of the fluorinated dimers.

Based on previous work that had been done in our lab[97] 3-heptanoylthiophene (**60**) was prepared as shown in Scheme 9 following the literature[98] method in which the Grignard reagent was reacted with an acid chloride in tetrahydrofuran (THF) at low temperature to produce the ketone.



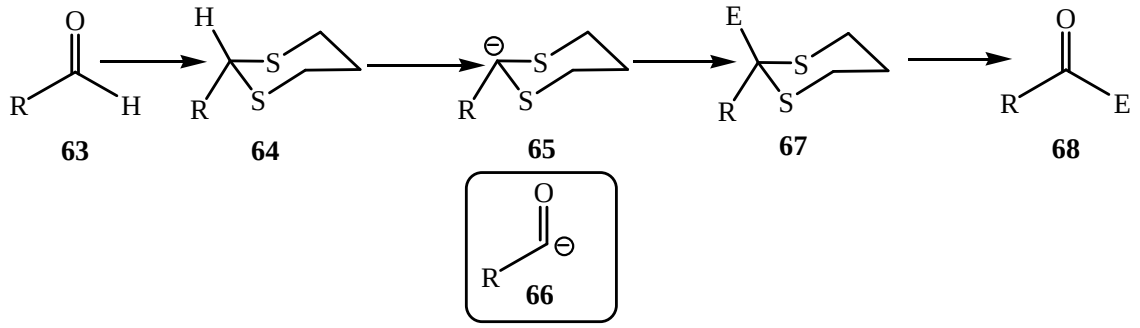
Scheme 9 Synthesis of 3-heptanoylthiophene (**60**) by the Grignard reaction

3-Thenoyl chloride (**61**) was synthesized in 93% yield by refluxing the thiophene-3-carboxylic acid (**62**) with an excess of $SOCl_2$ for 12 hours, the reaction was catalyzed by the addition of few drops of DMF. The Grignard reagent ($C_6H_{13}MgBr$) was prepared by the standard method in which the 1-bromohexane was refluxed with magnesium turnings for two hours in dry THF. The Grignard reagent was reacted with 3-thenoyl chloride (**61**) in THF at -78 ºC to generate 3-heptanoylthiophene (**60**) in 46% yield as a colorless liquid. The draw back of this synthetic method is the formation of tertiary

alcohol as a byproduct which was very hard to remove from the product during the purification process. In addition, this reaction required the use of a large excess amount of the thenoyl chloride (**61**) which makes this method relatively expensive to generate alkanoylthiophenes. This inspired us to pursue a better synthetic route.

*3.3.2 Synthesis of 3-heptanoylthiophene (**60**) by the reversible umpolung method*

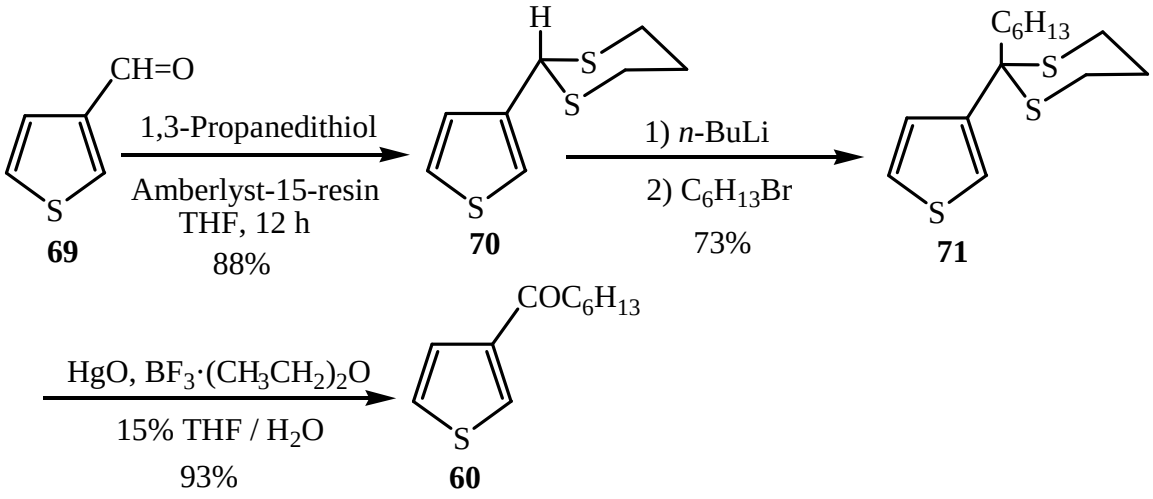
A different synthetic method was used to overcome the purification problem that we had encountered previously. In this method the polarity of the molecule was inverted (reversible umpolung) by the conversion of the aldehyde **63** to the thioketal (1,3-dithiane) **64**. The treatment of the thioketal **64** with butyllithium as shown in Scheme 10 led to the formation of the sulfur-stabilized anion **65** which is equivalent to the acyl anion **66**. The reaction of lithiodithiane **65** with an electrophile led to the formation of **67**. The carbonyl compound **68** was generated from the hydrolysis of **67**.[99,100]



Scheme 10 Synthesis of carbonyl compounds by reversible umpoloung method

This methodology was successfully applied in the preparation of 3-heptanoylthiophene (**60**) as shown in Scheme 11. Thiophene-3-carboxaldhyde (**69**) was treated with two equivalents of 1,3-propanedithiol in the presence of Amberlyst-15 resin to generate 2-thiophene-3-yl-(1,3)-dithian (**70**) in 88% yield. Metalation of the dithiane

70 with *n*-butyllithium followed by electrophilic quenching with hexylbromide led to the formation of 2-hexyl-2-thiophene-3-yl-(1,3)dithiane (**71**) in 73% yield. The hydrolysis of **71** with mercuric oxide and boron trifluoride etherate in THF led to the synthesis of 3-heptanoylthiophene (**60**) in 93% yield.



Scheme 11 Synthesis of 3-heptanoylthiophene (**60**)

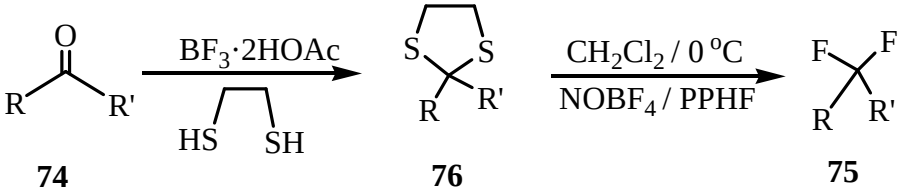
The advantages of this synthetic method include an improved overall yield of 58% relative to 42% and more importantly cleaner reactions and easier purification since no byproducts beside the starting material were observed. The product mixture (desired product and the starting material) were separated easily by means of flash chromatograpghy.

3.4 Synthesis of 3-(1,1-difluoroheptyl)thiophene (**72**) and 2,5-dibromo-3-(1,1-difluoroheptyl)thiophene (**73**)

The other key step in the synthetic route toward the preparation of fluorinated dimers is the conversion of the carbonyl oxygen of the ketone **74** into the corresponding difluoromethylene **75**. The fluorination of the ketone will be used as a model reaction for

the fluorination reaction in the synthesis of the dimers. Also the fluorinated thiophene is a monomer by itself and it is an interesting precursor for the conductive polymer.

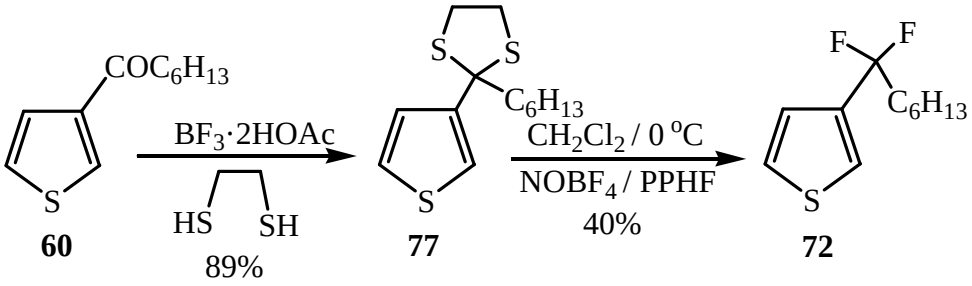
Several publications had been reported regarding the desulfurative fluorination of the dithiolane **76** into the corresponding difluoromethylene compound **75** using pyridinium polyhydrogen fluoride (PPHF) and nitrosonium tetrafluoroborate as shown in Scheme 12.[101-104]



74 **76** **75**

Scheme 12 The desulfurative fluorination of the dithiolanes

This synthetic methodology was applied in the synthesis of 3-(1,1-difluoroheptyl)thiophene (**72**) and this was accomplished as shown in Scheme 13.



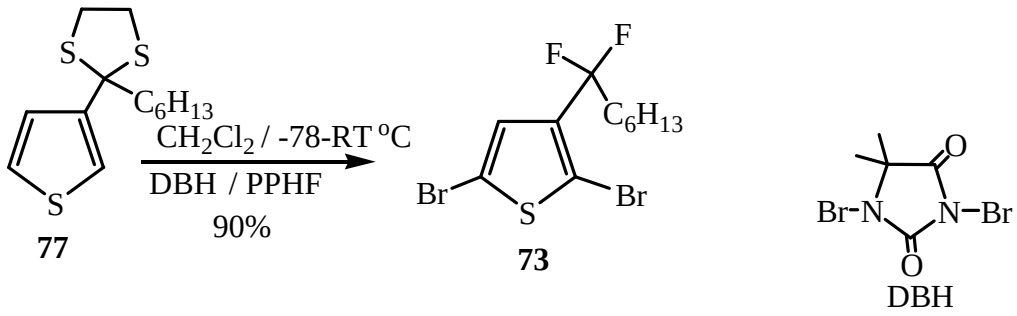
60 **77** **72**

Scheme 13 synthesis of 3-(1,1-difluoroheptyl)thiophene (**72**)

The 3-heptanoylthiophene (**60**) was converted to the 2-hexyl-2-thiophen-3-yl-1,3-dithiolane (**77**) by the reported method of Sondej,[105] in which boron trifluoride-acetic acid complex (BF_3•2HOAc) was used as the condensing agent and the solvent. The formation of **77** was afforded in 89% by the addition of one equivalent of BF_3•2HOAc

complex and two equivalents of 1,2-ethandithiol to the 3-heptanoylthiophene (**60**). The treatment of **76** with pyridinium polyhydrogen fluoride (PPHF) and nitrosonium tetrafluoroborate led to the formation of 3-(1,1-difluoroheptyl)thiophene (**72**) as a colorless liquid in 40% yield.

Interestingly, the treatment of **77** with pyridinium polyhydrogen fluoride in the presence of excess 1,3-dibromo-5,5-dimethylhydantoin (DBH) led to the formation of 2,5-dibromo-3-(1,1-difluoroheptyl)thiophene (**73**). The preparation of **73** was accomplished in one pot reaction in 90% yield as shown in Scheme 13. The dithiolane **77** was desulfurated, fluorinated and brominated in one step synthesis.



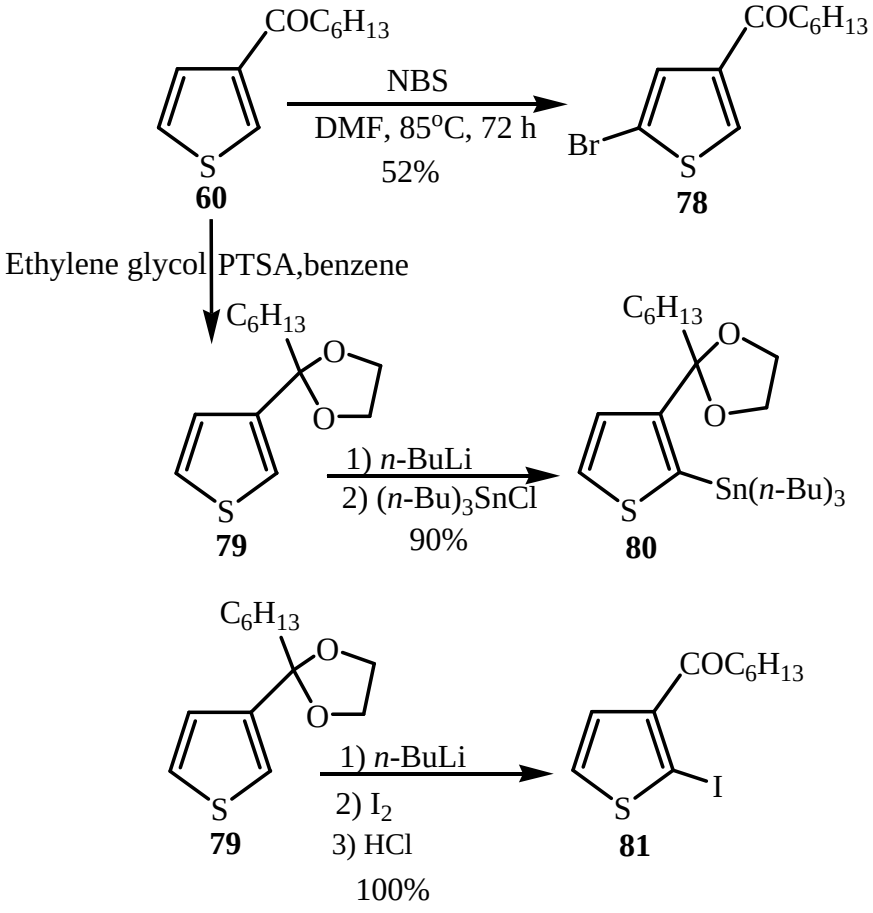
Scheme 14 Synthesis of 2,5-dibromo-3-(1,1-difluoroheptyl)thiophene (**73**)

It is worth noting that both **72** and **73** are monomers that upon polymerization could lead to formation of an interesting polymer. The corresponding polymer will have an advantage over the perfluorinated polymers. The alkyl chain is known to render the polymer soluble in most organic solvents[28] while the perfluoroalkylthiophene polymers are soluble only in critical carbon dioxide.[106-108]

3.5 Synthesis and study of head-to-tail 3,4'-bis(1,1-difluoroheptyl)-2,2'-bithiophene (**59**)

The Synthesis of head-to-tail 3,4'-bis(1,1-difluoroheptyl)-2,2'-bithiophene (**59**) as a model for the polymeric material was accomplished. The synthetic route includes the selective functionalization of the thiophene ring at the 2- and the 5-positions followed by the Stille coupling reactions prior to the fluorination reactions.

The synthesis started with the selective functionalization of 3-heptanoylthiophene (**60**) which was successfully accomplished as shown in Scheme 15.



Scheme 15 Functionalization of 3-heptanoylthiophene (**60**)

3-Heptanoylthiophene (**60**) was treated with one equivalent of N-bromosuccinimide (NBS) in N,N-dimethylformamide (DMF), the reaction mixture was heated to 80 °C for three days. The progress of the reaction was monitored by TLC (hexane-EtOAc, 4:1) which confirmed the complete consumption of the starting material after three days. 5-Bromo-3-heptanoylthiophene (**78**) was obtained in 52% yield. It is important to use only one equivalent of NBS since side products formed upon the use of more than one equivalent of NBS when we attempted to increase the rate of the bromination reaction. These side products made the purification process very difficult. This bromination reaction was used successfully in several similar systems in which the thiophene ring bears a carbonyl group was brominated selectively at the 5-position.

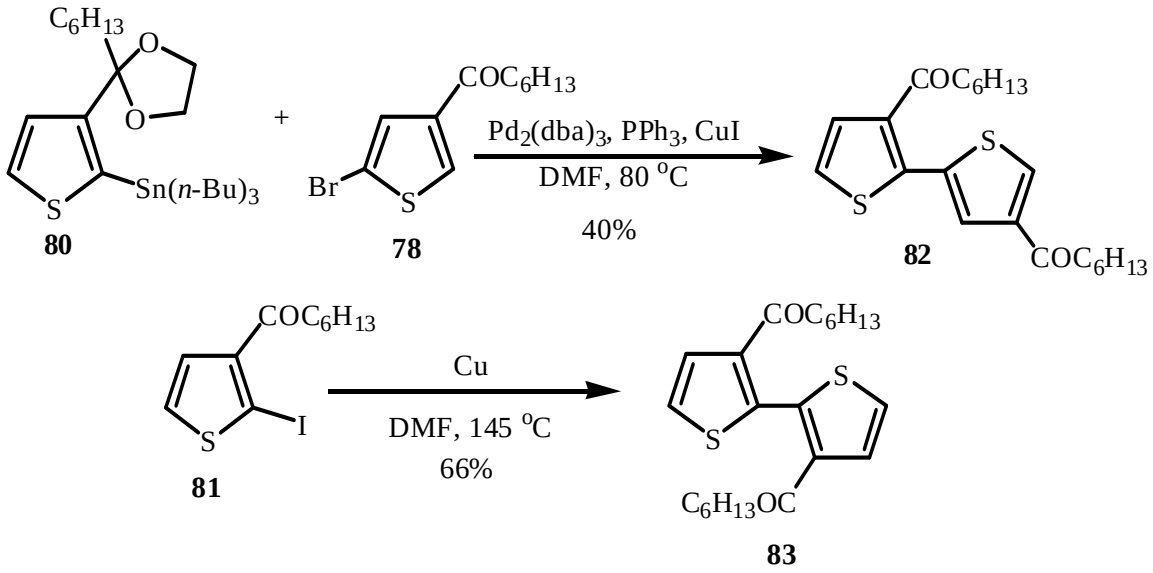
2-Hexyl-2-thiophen-3-yl-[1,3]dioxalane (**79**) was prepared by treating 3-heptanoylthiophene (**60**) with ethylene glycol and catalytic amount of *p*-toluenesulfonic acid in benzene. The mixture was heated under reflux in a round-bottomed flask connected to a Dean-Stark trap. The water-benzene azeotrope was continuously drained until it did not appear cloudy in about 6 hours. 2-Hexyl-2-thiophen-3-yl-[1,3]dioxalane (**79**) was treated with 1.10 equivalent of *n*-BuLi at -78°C and then quenched with tri-*n*-butylstannyl chloride which led to the synthesis of 2-(2- tri-*n*-butylstannylthiophen-3-yl)-2-hexyl-1,3-dioxolane (**80**) in 90% yield after the two steps. Compound **80** was used in the coupling reaction without further purification. The previous methodology was applied in several reactions in which the carbonyl group was transformed to the ketal which was treated with *n*-BuLi at -78° and quenched with the desired electrophile. This is a very

advantageous methodology which allows the selective substitution at the 2-position of the thiophene ring that bears a carbonyl group.

The previous methodology was applied to the synthesis of the 2-iodo-3-heptanoylthiophene (**81**) which was prepared by treating **79** with *n*-BuLi at -78°C and then was quenched with iodine. The reaction was monitored by the decoloration of the iodine. The product **81** was obtained in quantitative yield after the acid work up. Compound **81** was obtained as a colorless liquid which turned to dark upon standing probably because it decomposed and released iodine. It was not possible to obtain elemental analysis or MS data on this compound. Interestingly iodo-thiophenes are relatively stable at room temperature, although their color becomes dark upon standing for extended periods of time, which suggests slow decomposition. It is advantageous to use them when they are freshly prepared and store them at low temprature.

The synthesis of head-to-tail 3,4'-diheptanoyl-2,2'-bithiophene (**82**) was accomplished using the Stille reaction. The thiophene monomers, 5-bromo-3-heptanoylthiophene (**78**) and 2-(2-tri-*n*-butylstannylthiophen-3-yl)-2-hexyl-1,3-dioxolane (**80**), was coupled in the presence of $Pd_2(dba)_3$ (tris(dibenzylideneacetone)dipalladium(0)) (5%), triphenylphosphine (4 equivalents) and copper(I) iodide (10%). The head-to-tail 3,4'-bis(diheptanoyl)-2,2'-bithiophene (**82**) obtained in 40% yield as a pale yellow oil.

The head-to-head isomer 3,3'-diheptanoyl-2,2'-bithiophene (**83**) was prepared in 66% using the Ullmann coupling[96,109] in which 2-iodo-3-heptanoylthiophene (**81**) was reacted with freshly prepared copper powder[110] in dry DMF at 145 °C for 24 hours.



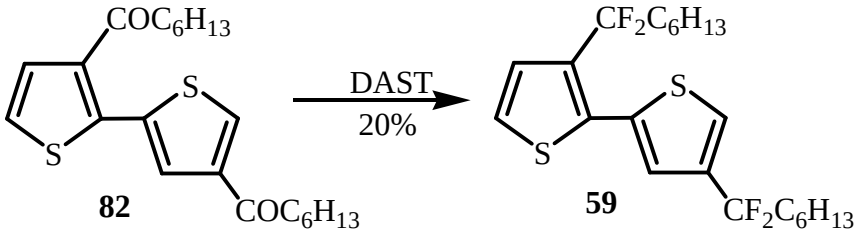
Performing the coupling reaction without activating the copper powder led to a poor yield of less than 10%.

Scheme 16 Synthesis of regioregular bi(heptanoylthiopene)s

Both dimers **82** and **83** were obtained as liquids which is unfortunate since the fluorinated dimers are anticipated to be liquids as well, and then the X-ray crystallography could not be performed on those molecules. The fluorination usually but not always leads to a drastic reduction in the melting point of the molecule.[103]

The H-T 3,4'-bis(1,1-difluoroalkyl)-2,2'-bithiophene (**59**) was prepared in 20% yield by the fluorination of **82** using DAST (diethylaminosulfurtrifluoride) as shown in Scheme 17. The low yield is typical for this reaction based on literature reports.[103,104] In these particular reactions mono-fluorination also contributes to the reduction of the yield. The attempt to solve this problem by increasing the amount of DAST and/or running the reaction for longer periods of time failed to increase the yield and led to difficulty in the

purification process since DAST seems to be decomposing to a black tar which was very hard to remove from the reaction mixture.



Scheme 17 Synthesis of head-to-tail 3,4'-bis(1,1-difluoroalkyl)-2,2'-bithiophene (**59**)

Unfortunately the H-T dimer **59** is a liquid and it was not possible to get the X-ray crystal structure. The solid state crystal structure is extremely important in order to determine the thiophene-thiophene dihedral angle, the two-dimension packing motif and the expected short distance between the fluorine atom and the sulfur atom on the adjacent thiophene ring.

Figure 3.1 shows the ^{19}F NMR spectrum of **59** which gives qualitative indication of the presence of the fluorine-sulfur interactions. The spectrum shows the expected two triplet peaks at -90.1 and -85.2 ppm. It is clear that the internal fluorine atoms closer to the sulfur atom of the adjacent thiophene ring were significantly shifted down field by 5.0 ppm compared to the external fluorine atoms. The external fluorine atoms have the same chemical shift as the monomer 3-(1,1-difluoroheptyl)thiophene (**72**). This indicates that these internal fluorine atoms are more positive than the terminal fluorine ones which suggest that intramolecular attractive interactions do exist between the fluorine atoms and the electropositive sulfur atom of the adjacent thiophene ring.

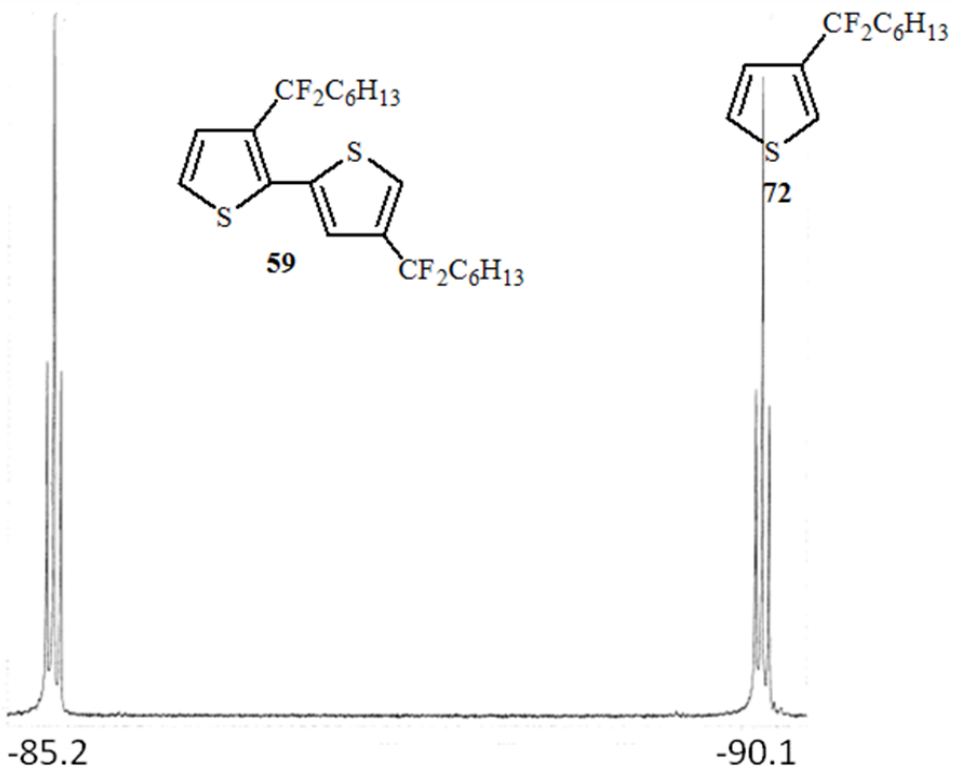
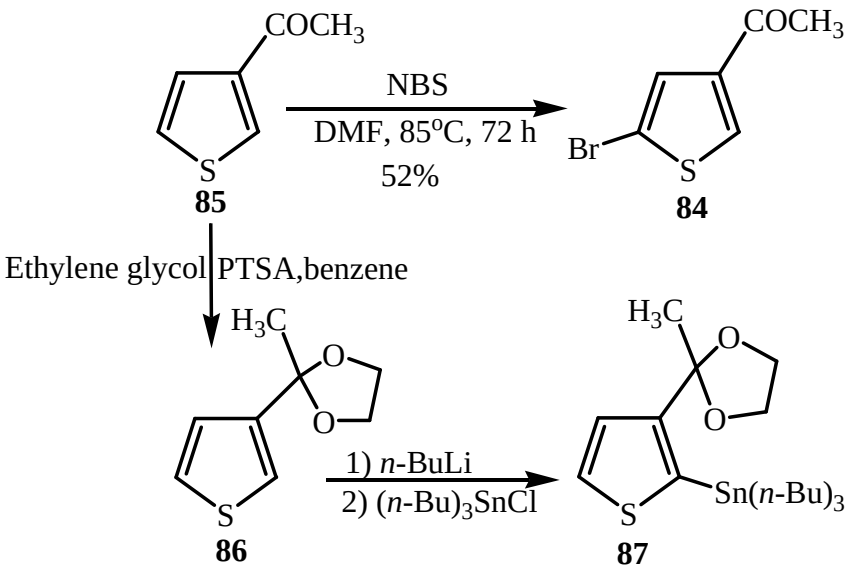


Figure 10 ^{19}F NMR spectrum of 3,4'-bis(1,1-difluoroalkyl)-2,2'-bithiophene (**59**)

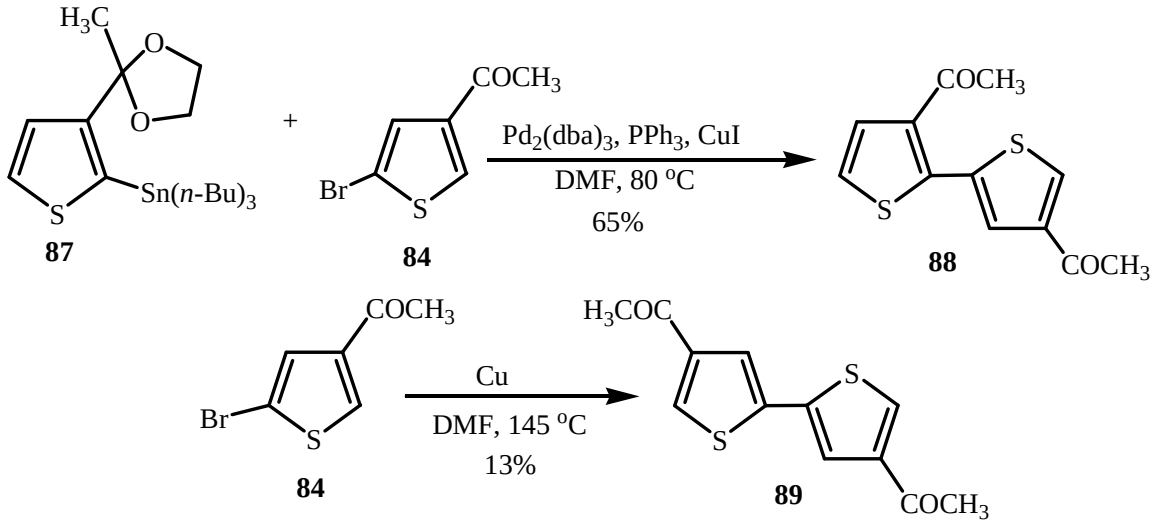
3.6 Synthesis of methylketone dimers

The next approach toward the synthesis of solid dimers was to reduce the length of the alkyl chain from the hexyl to the methyl ketone which might lead to solid dimers. The syntheses of the monomers are shown in Scheme 18. The syntheses are similar to the previous preparation of **82**. 5-Bromo-3-heptanoylthiophene (**84**) was prepared in 52 % yield by treating 3-acetylthiophene (**85**) with bromine in the presence of sodium acetate and glacial acetic acid. 2-Methyl-2-thiophen-3-yl-[1,3]dioxalane (**86**) was prepared similar to **79** and converted to 2-(2-tri-*n*-butylstannylthiophen-3-yl)-2-methyl-1,3-dioxolane (**87**) similar to the preparation of **80**.



Scheme 18 Functionalization of the 3-acetylthiophene (**85**)

The syntheses of H-T and T-T methylketone dimers were shown in Scheme 19.

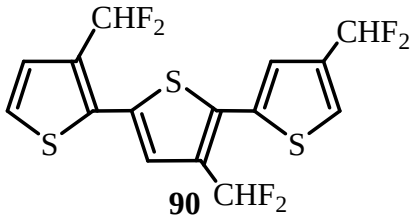


Scheme 19 Synthesis of the methylketone dimers

The Stille coupling reaction was performed in the preparation of the H-T 3,4'-diethanoyl -2,2'-bithiophene (**88**) which was obtained in 65% yield. The T-T isomer 4,4'-diethanoyl -2,2'-bithiophene (**89**) was prepared in 13% by the Ullmann coupling[96,109]

reaction in which 5-bromo-3-heptanoylthiophene (**84**) was treated with copper in DMF at 145 °C for two days. Both dimers **88** and **89** are solid with melting points 86-88 and 95-97 °C respectively. They showed poor solubility in organic solvents. The poor solubility in DAST led to a very poor yield of less than 10% of the fluorination reactions. The two dimers were obtained in a liquid mixture and it was not possible to completely purify them. The purifications were not pursued since a novel trimer was successfully prepared and the X-ray crystal structure was obtained.

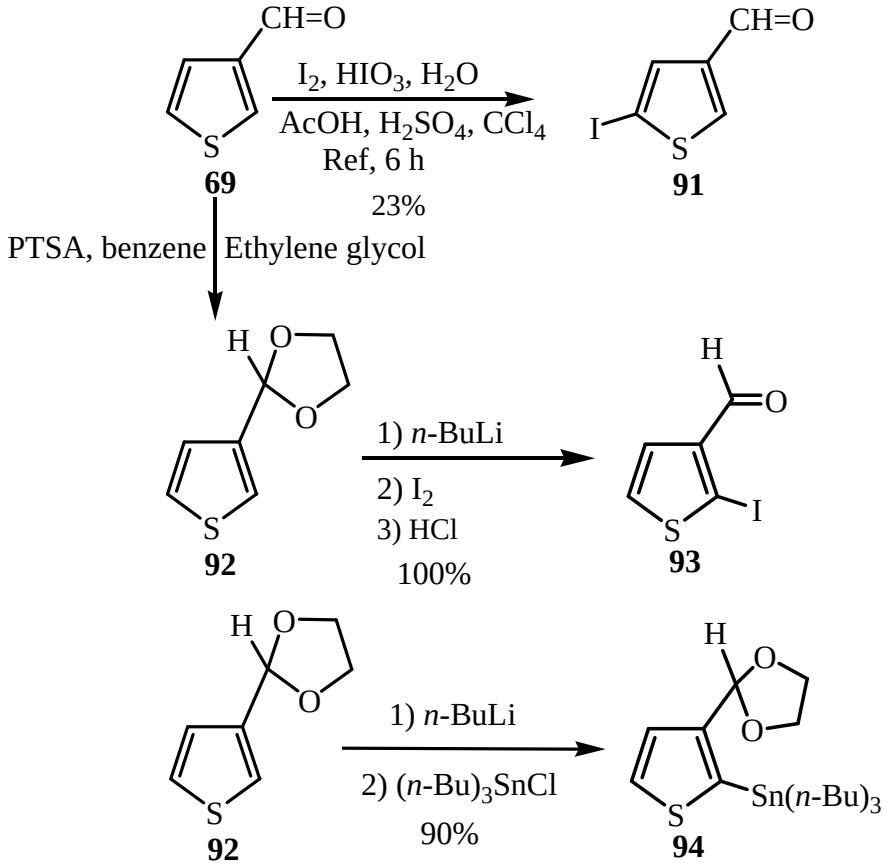
3.7 Synthesis of head-to-tail 3,4',4''-tris(difluoromethyl)-2,2':5',2''-terthiophene (**90**)



90

The next step is to design a synthetic route that possibly would lead to the formation of a solid fluorinated oligothiophene molecule which will enable us to obtain the X-ray crystal structure. This will give a clear view of the molecule and allow us to study the interesting features including possible inter- and intramolecular interactions, packing patterns and torsional angles. The choice is to prepare a thiophene trimer with shorter alkyl chain. Head-to-tail 3,4',4''-tri(difluoromethyl)-2,2':5',2''-terthiophene (**90**) is an ideal model since it has H-T regioregular linkages, it also has three thiophene units and contains difluoromethyl side-chains. The synthesis and study of the X-ray crystal structure of head-to-tail 3,4',4''-tri(difluoromethyl)-2,2':5',2''-terthiophene (**90**) will be discussed extensively below.

The synthetic route to the head-to-tail 3,4',4''-tri(difluoromethyl)-2,2':5',2''-terthiophene (**90**) begins with the selective functionalization of the thiophene ring at the 2- and the 5-postions as shown in Scheme 20. Thiophene-3-carboxaldehyde (**69**) was selectively iodinated at the 2- and the 5-posions. Thiophene-3-carboxaldhyde (**69**) was dissolved in CCl_4, H_2O, H_2SO_4 and acetic acid and was treated with 0.5 equivalent of iodine and HIO_3. The mixture was heated under reflux for six hours and the product, 5-iodothiophene-3-carboxaldehyde (**91**) was obtained in 23% yield.[111-113]

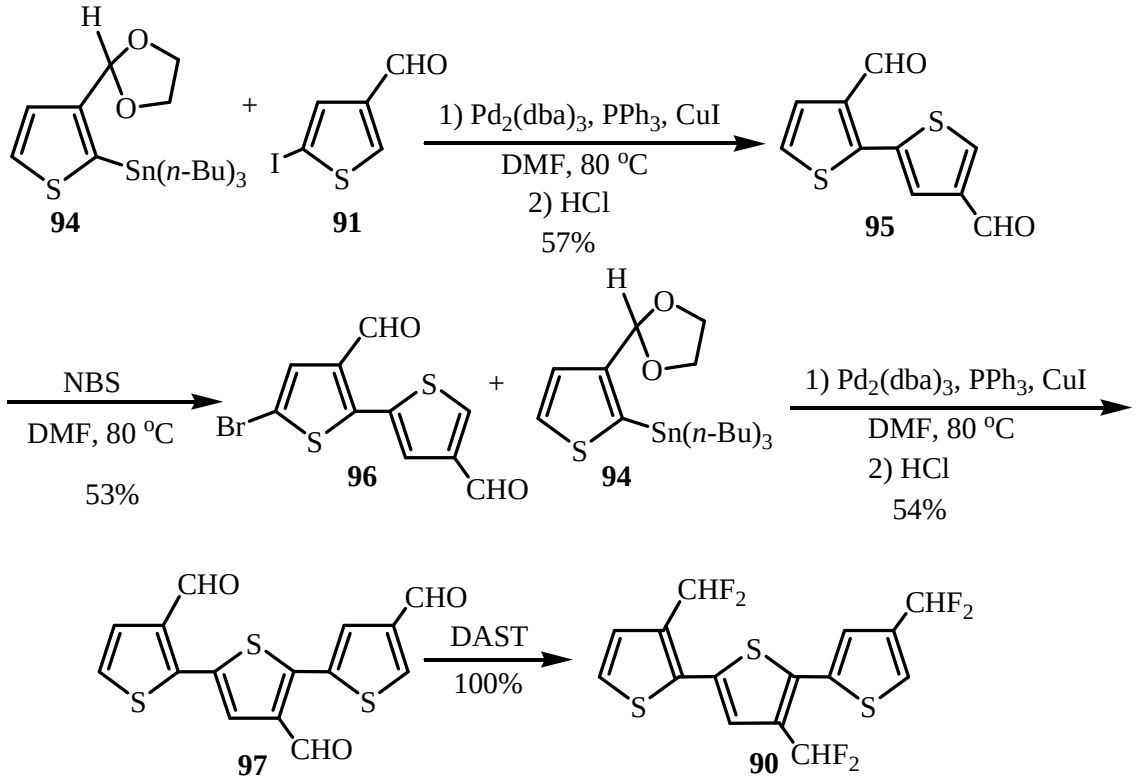


Scheme 20 Selective functionalization of thiophene-3-carboxaldehyde (**69**)

2-Thiophen-3-yl-[1,3]dioxalane (**92**)[114] was prepared in similar manner to **79** and treated with 1.1 equivalent *n*-BuLi at -78 °C which was quenched with iodine to afford

2-iodothiophene-3-carboxaldehyde (**93**) as a colorless solid in quantitative yield after the acid work up. 5-Iodothiophene-3-carboxaldehyde (**91**) and 2-iodothiophene-3-carboxaldehyde (**93**) are relatively stable at room temperature but they did partially decompose upon standing for long periods of time.

The synthesis of [3-(1,3-dioxolan-2-yl)thiophen-2-yl]tri-*n*-butylstannane (**94**) was accomplished in 90 % yield after the two steps similar to the preparation of **80**.



Scheme 21 Synthesis of 3,4',4''-tri(difluoromethyl)-2,2':5',2''-terthiophene (**90**)

The synthesis of 3,4',4''-tri(difluoromethyl)-2,2':5',2''-terthiophene (**90**) was accomplished as shown in Scheme 21. H-T 2,2'-bithiophene-3,4'-dicarbaldehyde (**95**) was prepared in 57% yield by Stille coupling reaction similar to the preparation of the ketone dimer **82**. The dimer **95** was brominated in 53% yield using NBS and DMF which led to

the preparation of 5-bromo-2,2'-bithiophene-3,4'-dicarbaldehyde (**96**). Dimer **96** was coupled with **94** to generate the H-T 3,4’,4’’-triformyl-2,2’:5’,2’’-terthiophene (**97**) in 54% yield. Trimer **97** was fluorinated using DAST which led to the formation of 3,4’,4’’-tris(difluoromethyl)-2,2’:5’,2’’-terthiophene (**90**) in quantitative yield.

These syntheses have several advantages over the previous ones. Excellent to good yields were obtained for all reactions, all compounds were very soluble in most organic solvents and the purification process was relatively easy. The fluorination reaction led to a quantitative yield over a relatively shorter period of time which is 24 hours compared to the ketone fluorination reactions that take four days and give moderate to low yield.

The regioregular H-T 3,4’,4’’-tris(difluoromethyl)-2,2’:5’,2’’-terthiophene (**90**) was obtained as a colorless solid which was crystallized and X-ray crystallography was performed on the molecule. This solves the problem we encountered earlier with H-T dimer **59** which was a liquid.

3.8 Study of the X-ray crystal structure of head-to-tail 3,4',4''-tris(difluoromethyl)-2,2':5',2''-terthiophene (**90**)

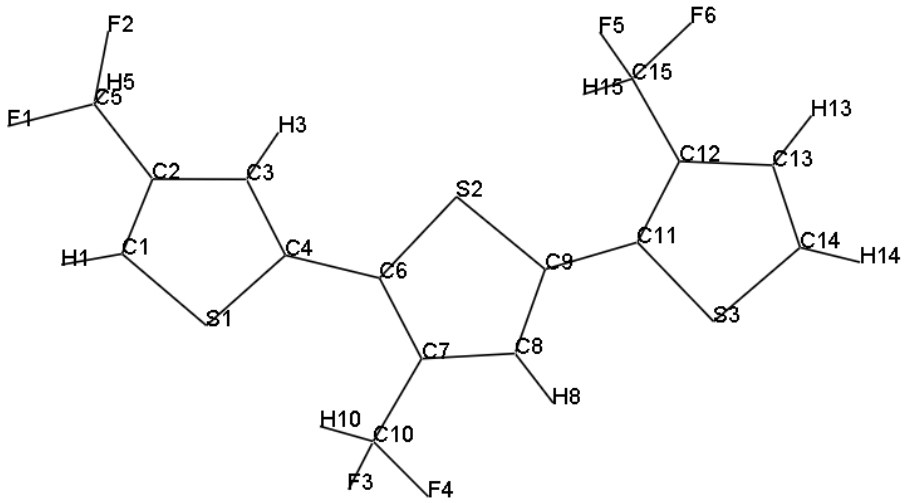


Figure 11 The single-crystal X-ray structure of **90**

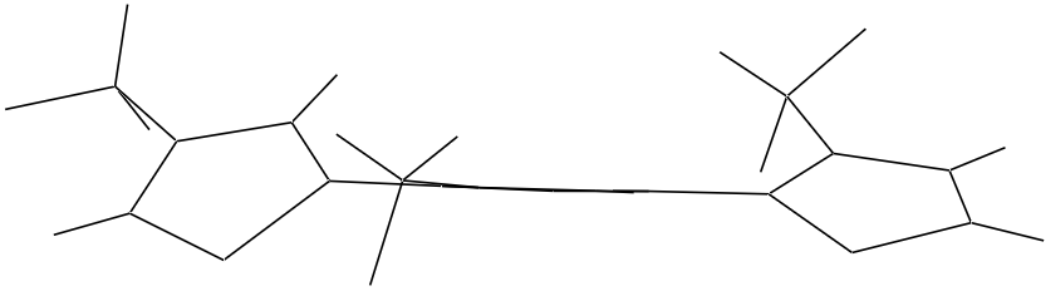


Figure 12 Side view of the single-crystal X-ray structure of **90**

Single crystals of the head-to-tail 3,4',4''-tris(difluoromethyl)-2,2':5',2''-terthiophene (**90**) was obtained by the recrystallization of **90** from the slow evaporation of ethylacetate:hexane (2:8). The single-crystal X-ray structure of **90** is shown in Figure

3.2. Figure 3.3 shows the side view of the molecular geometry which shows significant distortion from the co-planarity and it also shows the transoid conformations between the adjacent thiophene rings. The dihedral angle of S2-C9-C11-C12 is 28.2° and S1-C4-C6-C7 is 41.0°. The observed lager dihedral angle values compared to that of the 3,4',4''-trimethyl-2,2':5',2''-terthiophene (**13**) (dihedral angle: 7° and 7.8°)[42] could be due to the steric hindrance caused by the larger fluorine atoms (van der Waal radius: 1.47Å) that replaced the smaller hydrogen atoms (van der Waal radius: 1.09Å). The difference between the two dihedral angles (28.2 and 41.0°) does not affect the model study since the higher value represents the dihedral angle of the terminal thiophene ring of the corresponding polymer. The consecutive thiophene rings in the polymer should have dihedral angle values of 28.2°.

The crystal structure reveals several kinds of non-bonding S···F inter- and intramolecular interactions, and F···H short contacts do exist in this molecule. These interactions have a strong impact on the crystal packing motif of the molecule in the solid state.

Figure 3.4 shows the non-bonding interactions that do exist between the sulfur atom of the thiophene ring and fluorine atom from the adjacent molecule. This could be explained by the significantly shorter F···S distance of 3.07Å compared to the sum of the van der Waals radii which is 3.27Å. These F···S attractive interactions force one of the molecules to slide by one thiophene unit so the fluorine and the sulfur atoms come to close proximity as presented in Figure 3.4. An interesting feature of these F···S attractive interactions is that they force the two molecules to pack into a dimer through an inversion

center. The same dimeric behavior was observered in compound **21a** and **21b** in which the molecule is packed into a dimer through an inversion center as a result of O−H···F bonds.

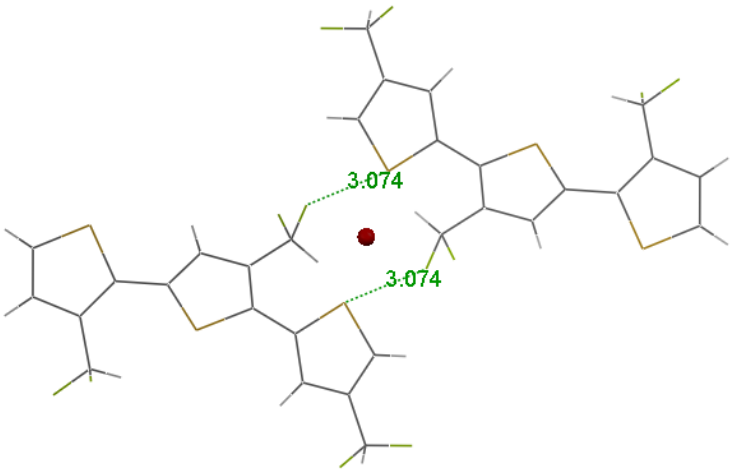


Figure 13 F···S intermolecular interactions

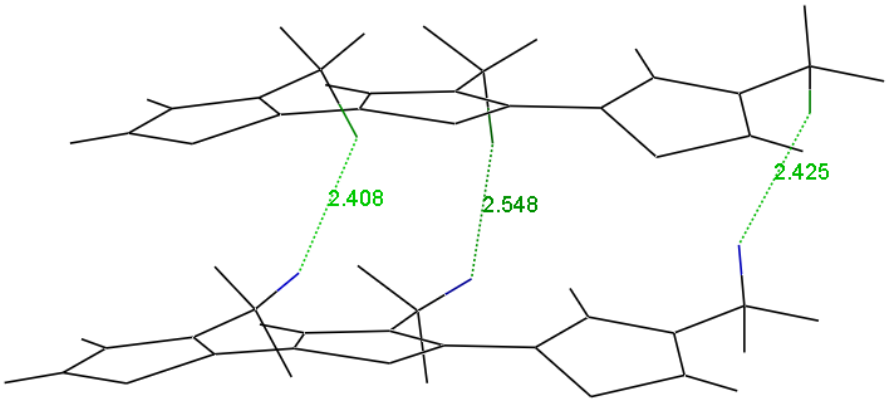


Figure 14 F···H intermolecular interactions

Figure 3.5 shows the F···H−CF_2 (hydrogen-bonding) intermolecular interactions that do exist between the fluorine atom of the thiophene ring and the hydrogen atom of the parallel molecule. The F···H short distance ranges from 2.40 to 2.55Å which is less than the sum of the van der Waals radii of the hydrogen and the fluorine atoms which is 2.56Å. The shorter F···H distance of 2.40Å (28.0°) causes the dihedral angle to be smaller realive to longer

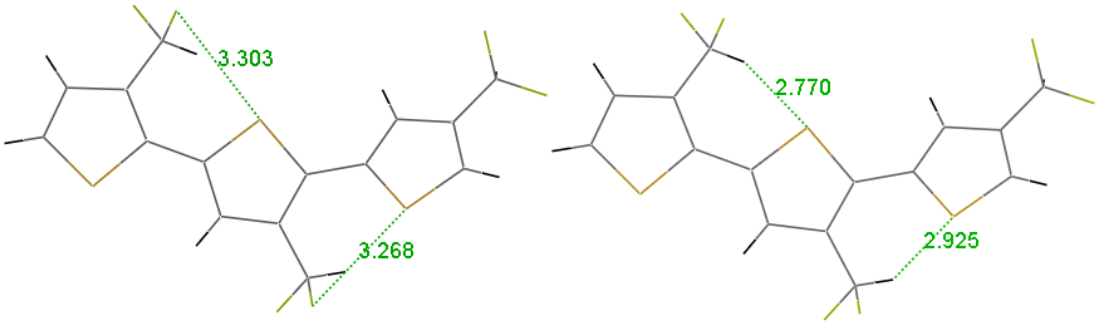


Figure 15 F···S intramolecular interactions (left) and S···H short contact (right)

Figure 3.6 (left) shows the non-bonding F···S intermolecular attractions. The F···S distance is 3.30Å which is close to the sum of the van der Waals radii of the sulfur and fluorine atoms which is 3.27Å. The short distance suggests that attractive interactions do exist between the electronegative fluorine atom and the sulfur atom of the adjacent thiophene ring which cause a decrease in the dihedral angle between the thiophene rings. These attractive forces also assist in the transoid geometry of the molecule. These interactions lead to a relatively larger dihedral angle (41.0°) of the thiophene ring that has a shorter F···S distance (3.27Å) which suggests that the molecule twists to allow the

fluorine and sulfur to become closer to each other. Figure 3.6 (right) also shows S···H short contacts of 2.77 and 2.93Å close to the sum of the van der Waals radii (2.79Å).

Another interesting feature of compound **90** is the supermolecular assembly in the solid state as shown in Figure 3.7. This is an extremely important feature of the molecule since the face-to-face π-stacking crystal structures of oligothiophenes are rarely reported in the literature due to the difficulty in the synthesis and growing single crystals.[36]

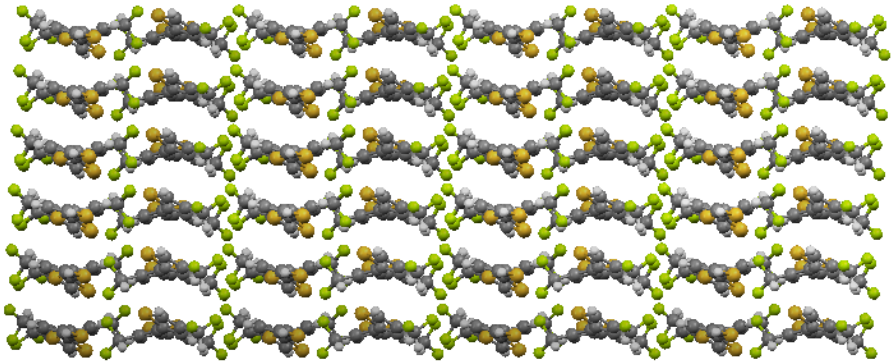


Figure 16 Molecular packing in the solid state of **90**

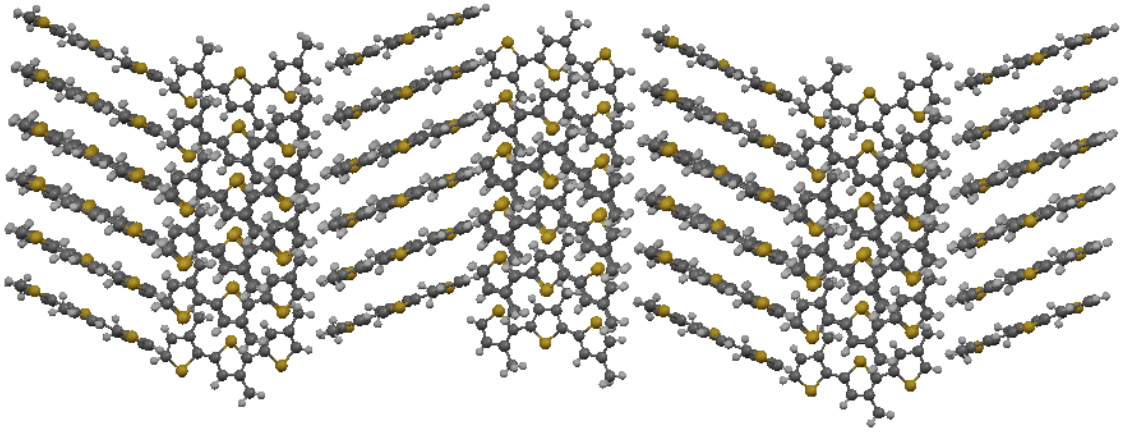


Figure 17 Molecular packing in the solid state of **13**

Figure 3.7 shows the crystal packing of **90** and Figure 3.8 shows the crystal packing of 3,4',4''-trimethyl-2,2':5',2''-terthiophene (**13**) in the solid state. The crystalline packing of **13** is a typical herringbone structure observed for non-fluorinated oligothiophenes.[33-37,42] In these systems the π−π interaction between the neighboring rings are minimized to reduce the repulsion between the π-orbitals which forces the layers to become perpendicular to each other. The crystal packing of **90** consists of face-to-face π-stacks of parallel molecules forming parallel layers to the ab plane. Interestingly, the crystal packing of **90** consists of successive stacks with essentially eclipsed thiophene rings which differ from the observed π-stack structures of fluorinated thiophenes in which the fluorinated thiophene rings are staggered with one side of the ring bisecting the successive molecule.[56,70] These molecules assembled in this fashion to offset the dipole moment induced by the fluorine atoms. We can conclude that the inter- and the intramolecular attractive forces that exist in this molecule overcome the dipole-dipole moment induced by the fluorine atoms which could be explained by the assembly of the thiophene rings of the successive layers in eclipsed geometry. Also, the π−π attractive interactions between the thiophene rings of the adjacent molecules lead to the face-to-face packing motif.

An interesting feature of the molecule **90** is the alignment of all atoms: fluorine atoms, sulfur atoms and hydrogen atoms in a perfect mirror to each other as shown in Figure 3.9. The consecutive layers were separated by short distance of 4.0Å (TMT **13**: 5.35Å).

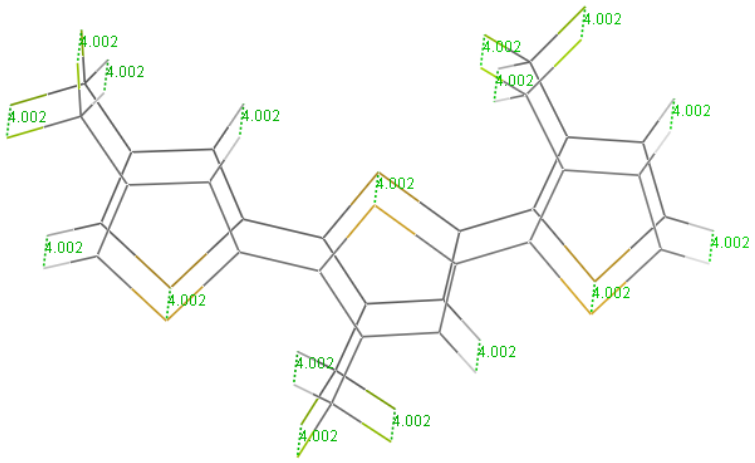


Figure 18 The short stacking distance between the consecutive layers

3.9 The implications of the crystal-packing structure of **90** into future applications

Figure 3.9 shows schematic diagram of an OFET (organic field-effect transistors) device. The main components of this device are the source-drain, semiconductor, dielectric and the gate. In this device a thin film of the organic semiconductor is deposited on the top of a dielectric with an underlying gate electrode.[115-117] Oligo and polythiophenes are among the most extensively investigated organic semiconductors used in OFET devices.[118-120] The vast majority of these materials are p-type, meaning that the semiconductor acts as a hole-transporting material.[121-124] To date very little is known about n-type electron transporting materials. One of the most effective ways to facilitate the electron injection which lead to an increasing n-type character is the introduction of electron-withdrawing groups into the π-conjugated system.[106,125] The introduction of an electron-withdrawing group like fluoro or fluoroalkyl substituents into the π-conjugated systems stabilizes the LUMO energy level which facilitates the electron injection, leading

to an efficient n-type semiconductor.[70,126-129] Fluorine is the most electronegative atom among all elements and therefore fluoroalkyl polythiophenes are ideal candidates for n-type semiconductors.

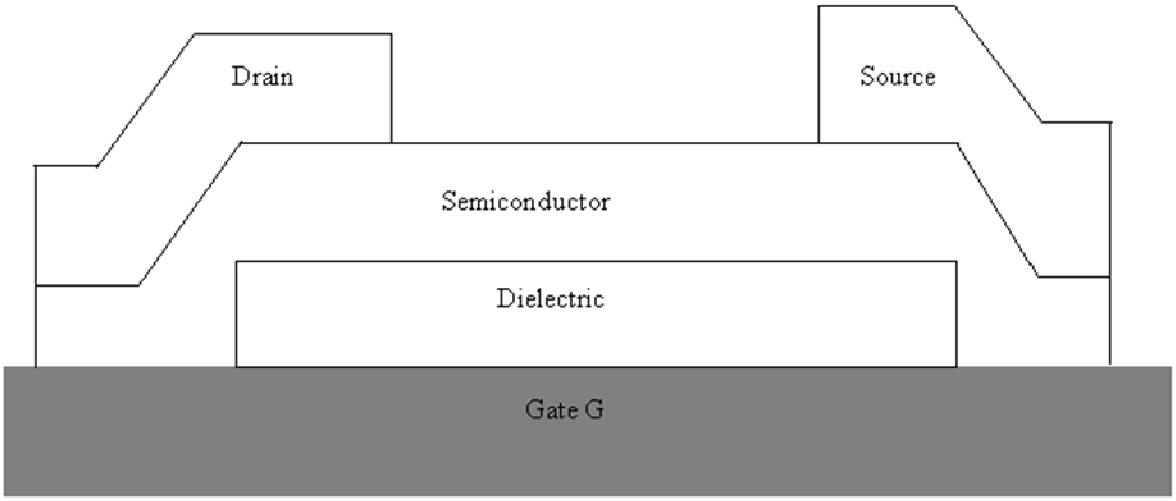


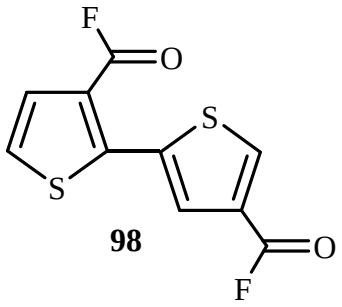
Figure 19 Schematic diagram of an OFET device

The head-to-tail 3,4',4''-tris(difluoromethyl)-2,2':5',2''-terthiophene (**90**) offers an excellent model for an n-type semiconductor mater that could be used in OFET devices. This molecule has the following features i) the electron-withdrawing fluoroalkyl group attached to the thiophene ring lowers the LUMO levels which facilitate the electron injection which creates an efficient n-type semiconductor, ii) the H-T regioregularity of the molecule minimizes the steric hindrance which insures the highest electron mobility. The H-H linkages are highly twisted and act as charge traps which severly reduces the charge mobility, iii) the face-to-face packing motif maximizes the π-π overlap between the adjacent molecules which results in high charge mobilities in the two-dimensional layers. The combinations of these features with the unique

characteristics of the fluorinated material like hydrophobicity, thermal stability, chemical and oxidative resistance makes this molecule a novel model from a scientific and industrial prospectives.

3.10 Synthesis and study of 2,2'-bithiophene-3,4'-dicarbonyl difluoride (**98**)

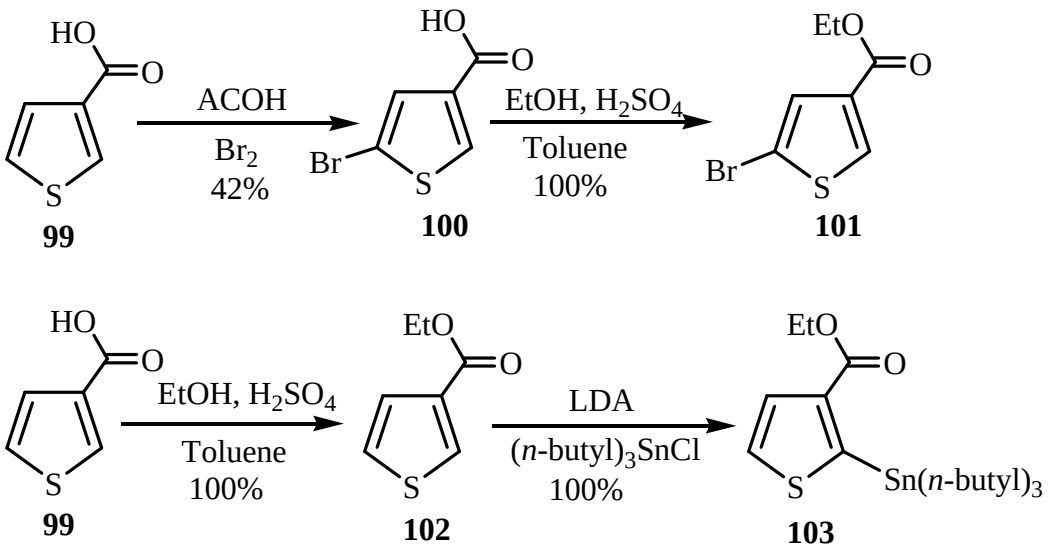
In the previous chapter the inter- and intra molecular F···S interactions that do exist in trimer **90** were discussed. Our efforts continued toward the study of the attractive forces that exist between the carbonyl oxygen atom and the sulfur atom on the adjacent thiophene rings, which induces planarity in the molecule and has an impact on the crystal packing in the solid state. The next target is to design a system that has both the fluorine and the carbonyl oxygen in the same molecule.



98

2,2'-Bithiophene-3,4'-dicarbonyl difluoride (**98**) is an interesting molecule since it has two competitive electronegative atoms, each of which could rotate and attract the sulfur atom. The influence of two electronegative atoms on the crystal packing of the molecule in the solid state will be investigated. The synthesis of 2,2'-bithiophene-3,4'-dicarbonyl difluoride (**98**) was accomplished.

The synthesis of the thiophene monomers was accomplished as shown in Scheme 22.

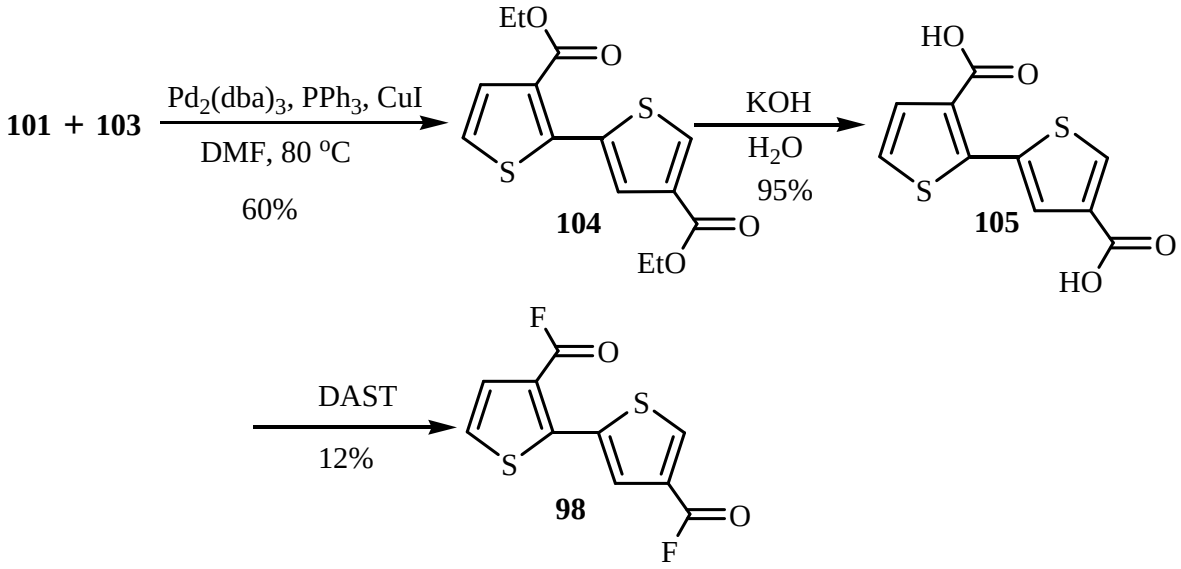


Scheme 22 Synthesis of the thiophene monomers

Thiophene-3-caroxylic acid (**99**) was brominated[109] to give 2-bromothiophene-4-carboxylic acid (**100**) in 42% yield, followed by esterfication[130] to afford ethyl 2-bromo-thiophene-4-carboxylate (**101**) in quantitative yield. The esterfication of thiophene-3-carboxylic acid (**99**) led to the formation of ethyl thiophene-3-carboxylate (**102**) in quantitative yield, and this was treated with lithium diisopropylamine, then quenched with tri-*n*-butyltin chloride to give ethyl 2-(tri-*n*-butylstannyl)thiophene-3-carboxylate (**103**) in quantitative yield.

The synthesis of the dimers is shown in Scheme 23. The H-T dimer, diethyl 2,2'-bithiophene-3,4-dicarboxylate (**104**) was prepared in 60% yield using the Stille reaction, in which ethyl 2-(tri-*n*-butylstannyl)thiophene-3-carboxylate (**103**) was coupled with ethyl 2-bromo-thiophene-4-carboxylate (**100**) in the presence of copper(I) iodide, triphenyl phosphine and $Pd_2(dba)_3$. Dimer **104** was saponified with KOH to generate the 2,2'-bithiophene-3,4-dicarboxylic acid (**105**) in 95% yield. Dimer **105** was fluorinated

with DAST which led to the formation of the H-T acid fluoride dimer **98** as a white solid in 12% yield. The low yield is attributed to high reactivity of the acid fluoride dimer **98** which decomposed during the work up process. The TLC showed a complete conversion of **104** to **98** prior to the work up. Unfortunately small crystals were obtained and the x-ray crystal structure was not possible at this time.



Scheme 23 Synthesis of H-T 2,2'-bithiophene-3,4'-dicarbonyl difluoride (**98**)

3.11 Conclusion

Fluorinated thiophene monomers, dimers and trimers were prepared. The synthesis of 3-heptanoylthiophene (**60**) by reversible umpolung methodology was accomplished. This methodology led to an improved overall yield, cleaner reactions and easier purification process. The synthesis of 3-(1,1-difluoroheptyl)thiophene (**72**) was accomplished. This is an interesting monomer which could be used to obtain a novel conducting polymer. This monomer contains the alkyl side chain that renders the

corresponding polymer soluble in organic solvents, which is necessary for the processing of the polymer. This fluorinated polymer is anticipated to have remarkable features such as high thermal and oxidative stability, a relatively higher hydrophobicity and lipophobisity in combination with the electrical conductivity. The synthesis of head-to-tail 3,4'-bis(1,1-difluoroalkyl)-2,2'-bithiophene (**59**), a model for the corresponding polymer, was accomplished. Unfortunately, this dimer was a liquid and we were not able to obtain its crystal structure. This was motivation for the preparation of the novel molecule, head-to-tail 3,4',4''-tri(difluoromethyl)-2,2':5',2''-terthiophene (**90**) which was crystallized and studied. This trimer revealed interesting inter- and intramolecular fluorine-sulfur interactions that shaped the molecule in the solid state. Based on the structural features and packing style, this molecule is an excellent model for an n-type oligomer or polymer semiconductor. The two-dimensional face-to-face π-stacking motif is very advantageous for high charge mobility which makes the corresponding oligomer an ideal candidate for OFET devices.

CHAPTER 4

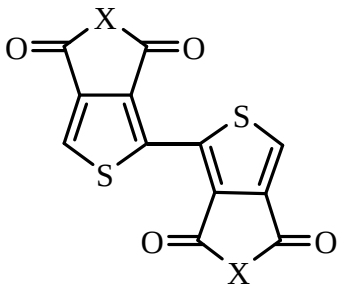
AN APPROACH TOWARD THE SYNTHESIS OF FLUORINATED BI(CYCLOPENTA[*c*]THIOPHENE)S

4.1 Overview

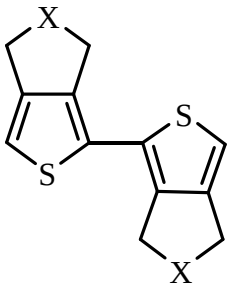
In the previeous chapter the X-ray crystal structure of head-to-tail 3,4',4''-tri(difluoromethyl)-2,2':5',2''-terthiophene (**90**) was obtained. The dihedral angle between the H-T linkages of the molecule was about 28.0° which is significantly distorted from planarity, however, this does not alter the packing motif. The next target is an attempt to reduce the dihedral angle without disturbing the face-to-face crystal packing motif in the solid state which is crucial to the performance as organic semiconductor. Table 3 shows that the incorporation of a fused five-membered ring into the thiophene ring caused a significant shift of the optical spectrum to a higher λ_{max}. The data showed that the λ_{max} of poly(cyclopenta[*c*]thiophene) (**17**) is 610 nm which is higher than the λ_{max} (450 nm) of poly(3-methylthiophene) (**9**). It is clear that the five-membered ring has induced planarity in the polymer despite the fact that the thiophene ring becomes disubstituted.

The incorporation of the C=O into a five-membered ring fused to the thiophene ring was proven to be an efficient method to reduce the steric effect and induce planarity of the system. 3-21G* Quantum mechanical calculations on several five-membered ring

systems (**106-113**) demonstrated that these molecules are essentially planar because of the interamolecular sulfur-oxygen interactions.[94]



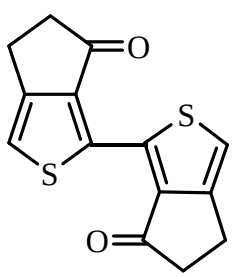
106: X = O
107: X = S
108: X = NCH_3
109: X = CH_2



110: X = O
111: X = S
112: X = NCH_3
113: X = CH_2

The calculations[94] revealed interesting results; compounds **106-109** were all planar despite the fact that the two carbonyl groups were in H-H arrangements. These results contrasted with the open chain H-H isomer **55** which has a dihedral angle of 74.8°. The replacement of the carbonyl group with CH_2 group as shown in compounds **110-113** led to considerably twisted systems. Apparently, the molecules **106-109** are planar because of the intermolecular S···O interactions which overcomes the steric effect caused by the carbonyl groups H-H linkages. In addition, the sulfur-oxygen distances in compounds **106-109** were 2.896, 2.709, 2.876, and 2.792 Å respectively, while the sulfur-hydrogen distances in compounds **110-113** were 3.117 and 3.190 Å in **110**, 3.404 and 3.696 Å in **111**, 3.110 and 3.223 Å in **112** and 3.219 and 3.334 Å in **113**. In compounds **106-109** the distance between the oxygen and the sulfur is significantly smaller than 3.22 Å, which is the sum of the oxygen and sulfur van der Waals radii.[94,95] On the other hand, the sulfur-hydrogen distances in compounds **109-113** were significantly larger than the

sum of the sulfur-hydrogen van der Waals radii which is 2.79 Å. The short sulfur-oxygen distances are the result of the intermolecular attractive forces between the two atoms.



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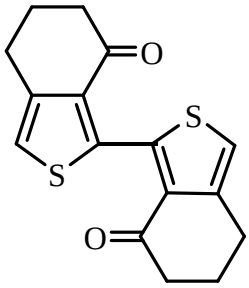

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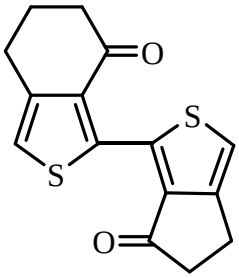
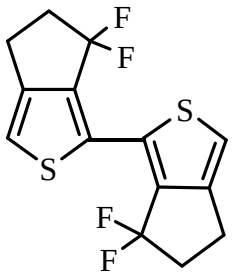


116

The calculations (3-21G*) on the diketones **114**-**116** also showed that diketone **114** is the only planar molecule. The conversion of the five-memebered rings into six-membered rings led to extremely twisted molecule. The dihedral angle of the six-membered ring diketone **115** is 80.2°. The diketone **116** which has one five-membered ring and another six-membered ring is considerably twisted with dihedral angle of 68.5°.[94,95] It is clear that the five-membered ring systems are relatively more planar than the six-membered ring systems. In addition, the substituent effect should be taken into consideration when designing such molecules. A delicate balance between the steric and electronic effect will lead to molecules with very interesting features.

We attempted to synthesize and study systems in which fluorinated five-membered rings will be fused to the thiophene rings. The fluorinated H-H and H-T compounds **117** and **118** are ideal candidates to study the effect of the incorporation of the fluorinated five-membered-ring on the planarity of the molecule and the crystal packing in the solid state. The 2-dimentional crystal packing motif in the solid state has an important impact on the charge mobility through the system.



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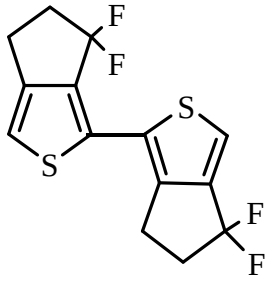
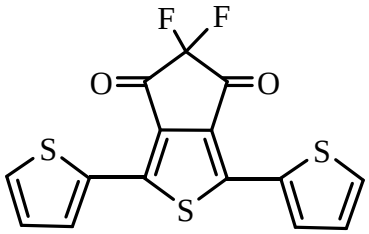


118

The synthesis and the crystal structure of similar structures have been reported recently.[126,129,131]



119

The crystal structure of compound **119** showed three independent molecules in the unit cell. All of these molecules adapted the trans conformation geometry in which the consecutive sulfur atoms are anti to each other. Interestingly, the dihedral angles are different from one molecule to another. The dihedral angle values ranges from 1.0 to 18.7°. It is worth noting that one of the molecules is nearly planar with dihedral angles ranges from 1.0 to 1.6°, the second molecule has dihedral angles ranges from 2.7 to 5.0° and the third molecule has dihedral angles ranges from 7.9 to 18.1°. The sulfur-oxygen distances of these molecules ranges from 2.96 to 3.04 Å which are slightly higher than the calculated values of the non-fluorinated molecules **103**-**108**, but these values are still smaller than the sum of the van der Waals radii of the sulfur and oxygen which is 3.22 Å.

It is clear that the intermolecular sulfur-oxygen interactions overcome the steric effect by enforcing the trans geometry.

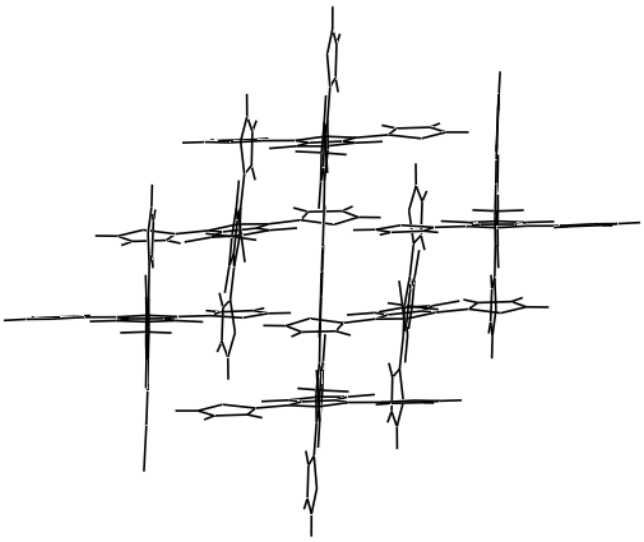
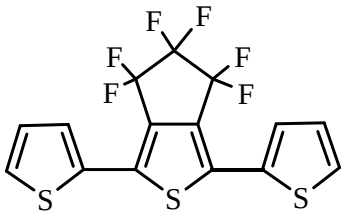


Figure 20 The crystal packing of **119** in the solid state

The crystal packing motif of **119** in the solid state is shown in Figure 4.1 which showed a slipped face-to-face stacking style typical for fluorinated compounds. The crystal packing in the solid state shows that the layers stack perpendicular to each other which is disadvantageous for high charge mobility. This might be ascribed to the excessive fluorination of the five-membered ring which arranged to cancel the dipole interaction between the perfluorinated five-membered rings.

The X-ray crystal structure of **120** and **121** also were reported. The molecules adapted the cis conformation in which the consecutive sulfur atoms are syn to each other. This could be due to lack of the sulfur-fluorine intrarmolecular interactions compared to **119** which has the transoid geometry due to the sulfur-oxygen interactions. The dihedral angle of **120** is around 30.0° and the dihedral angles for **121** are 25.5 and 22.1°. These

values are comparable to the dihedral angle of the open chain trimer **90** which has a dihedral angle of 28.0°. This could be attributed to steric hindrance caused by the perfluorination which overcomes the sulfur-fluorine attractive interactions.



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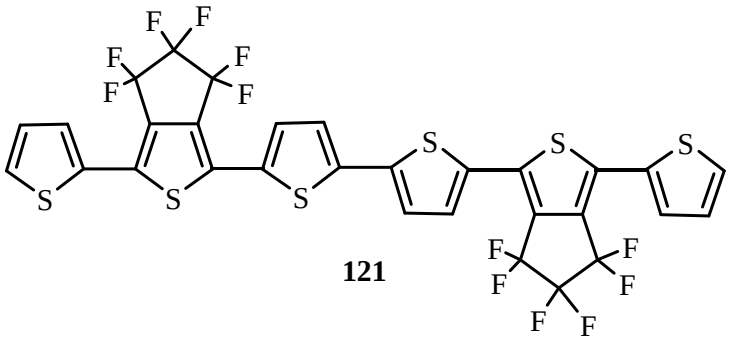
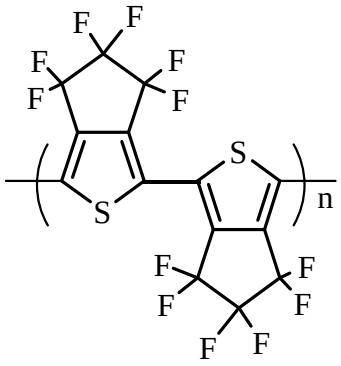


121

The crystal packing motif of **120** and **121** in the solid state is similar to that of **119** in which they showed a slipped face-to-face stacking style typical for fluorinated compounds. Also the crystal packing in the solid state shows the layers stack perpendicular to each other which is disadvantageous for high charge mobility.



122 n=1
123 n=2
124 n=3

The synthesis of dimer **122**, tetramer **123** and hexamer **124** was reported. Unfortunately, the X-ray crystal structures were not obtained for these molecules. The UV-vis data showed that absorption maximum red shifted and the molar extinction coefficient increased as the number of thiophene units increased as shown in Table 6.[129]

The π-π* transition energies of these molecule showed a linear relation against the inverse thiophene units which indicates that the incorporation of the fluorinated five-membered ring into the thiophene ring did not disrupt the effective conjugation of the oligomer.

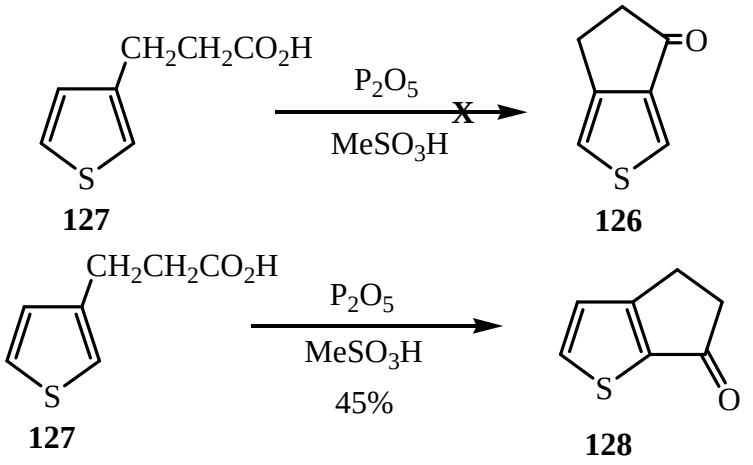
Table 6 UV-vis absorbtion and molar extinction coefficient data

Oligomer	λ_{max} (THF) (nm)	molar extinction coefficient ε
122	312	16000
123	376	27000
124	398	33000

The previous discussion showed that the incorporation of the five-membered ring into the thiophene ring led to a significant reduction of the dihedral angle compared to the open chain H-H isomer. The presence of carbonyl groups was special and led to completely planar molecules even though the carbonyl groups were in H-H arrangements. Although these calculations are extremely important when it comes to design of polythiophenes, they do not provide the details of crystal packing in the solid state. The syntheses and the X-ray crystal structure of these molecules will provide insight and an overview of the molecular packing in the solid state. It is also worth noting that the full perfuorination of the five-membered ring led to relatively hindered molecules and a disadvantageous molecular packing.

4.2 Synthesis of the 1,3-dichloro-4,4-difluoro-5,6-dihydrocyclopenta[*c*]thiophene (**125**)

The synthesis of 5,6-dihydrocyclopenta[*c*]thiophen-4-one (**126**) is the key precursor in the synthetic approach toward the preparation of the dimers. The selective functionalization of this monomer at the 2- and the 5-position will be crucial to the coupling reaction in the preparation of the dimers. Unfortunately the direct preparation of the ketone **126** turned out to be far from being straight forward as shown in Scheme 24.

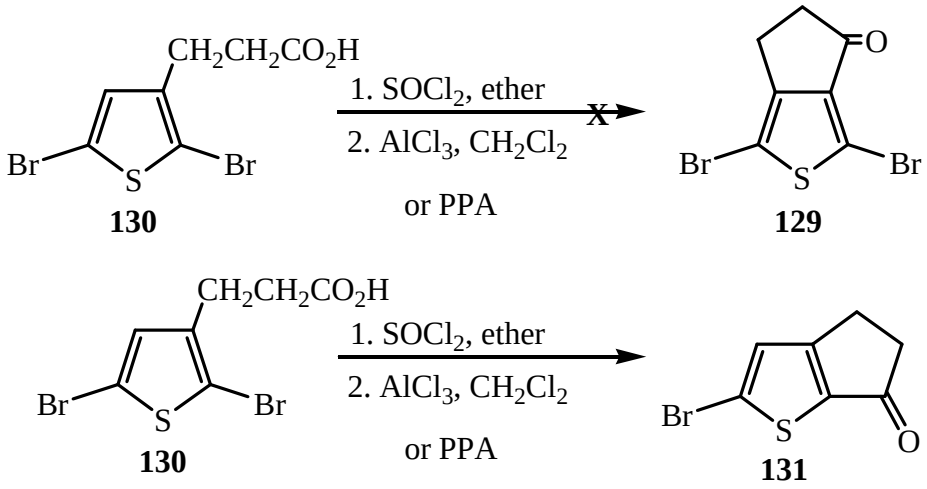


Scheme 24 Attempted syntheses of 5,6-dihydrocyclopenta[*c*]thiophen-4-one (**126**)

The treatment of 3-(thiophen-3-yl)propanoic acid (**127**) with P_2O_5 in methanesulfonnic acid led exclusively to the formation of the 2,3-fused system **128**.[132]

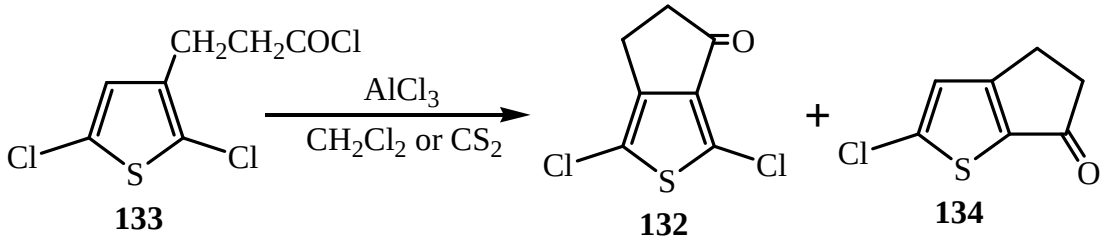
In an earlier report the attempted preparation of the dibromoketone **129** by heating 3-(2,5-dibromothiophen-3-yl)propanoic acid (**130**) with polyphosphoric acid (PPA) also led to cyclization at the 2-position of the thiophene ring (dibromoketone **131**) as shown in Scheme 25.[133] Bromine is not an effective blocking group in the reactive

alpha positions under Friedel-Craft conditions and it is readily undergoes electrophilic substitution.[132,133]



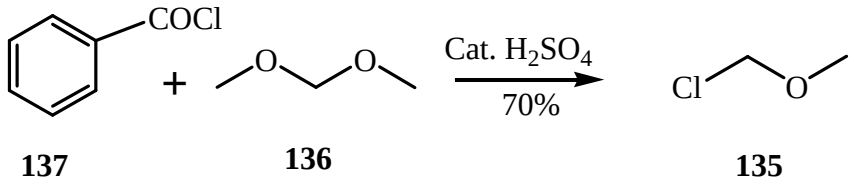
Scheme 25 Attempted syntheses of dibromoketone **129**

The preparation of the 1,3-dichloro-5,6-dihydrocyclopenta[*c*]thiophen-4-one (**132**) was reported in the literature.[134] Chlorines were proven to be an efficient blocking group. Under the Friedel-Craft reaction conditions, the treatment of the acid chloride (**133**) with aluminum trichloride as shown in Scheme 26 afforded the 3,4-fused ring ketone **132**. This reaction led to the formation of minor amounts of the 2,3-fused ring system **134**. This synthetic method was followed in preparation of the dichloroketone **132** and will be discussed in the following paragraphs.



Scheme 26 The successful synthesis of the dichloroketone **132**

The synthetic route started with synthesis of chloromethyl methyl ether (**136**) as shown in Scheme 27, which was prepared according to the literature method.[135] Chloromethyl methyl ether (**135**) was prepared in 70% yield by treating dimethoxymethane (**136**) with benzoyl chloride (**137**) in the presence of catalytic amount of sulfuric acid. Large scale synthesis involved 2 moles of the starting material led to the formation of 112 g of chloromethyl methyl ether (**135**). ^{1}H NMR spectroscopy ($CDCl_3$) showed that there was 6% of dimethoxymethane (**136**) in the product (δ 3.35 and 4.56 ppm, lit.[135] δ 3.34 and 4.56 ppm). It is worth noting that this preparation is considerably cheaper than the commercial material.

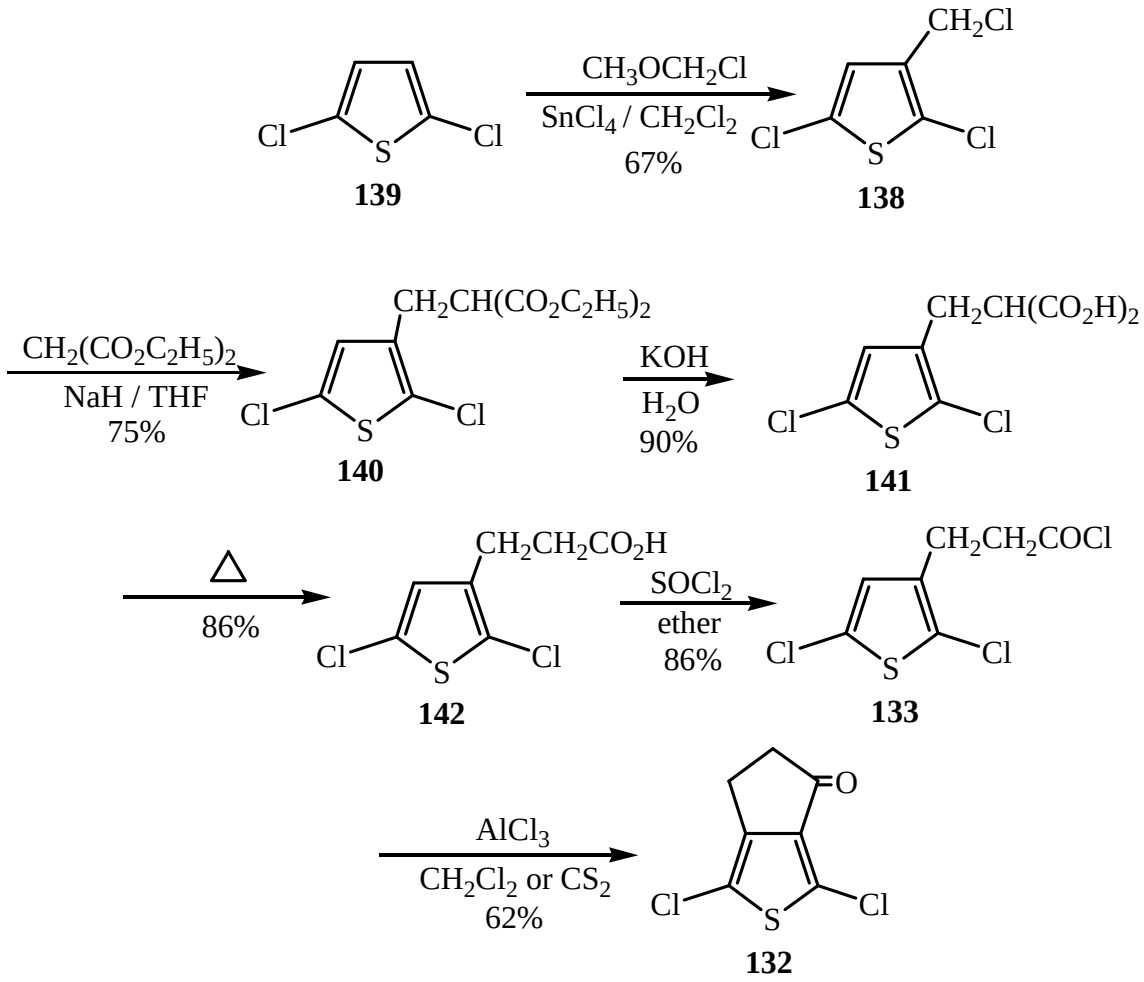


137 **136** **135**

Scheme 27 Preparation of chloromethyl methyl ether (**135**)

1,3-Dichloro-5,6-dihydrocyclopenta[*c*]thiophen-4-one (**132**) was prepared as reported.[134,136] 3-Chloromethyl-2,5-dichlorothiophene (**138**) was prepared by treating 2,5-dichlorothiophene (**139**) with chloromethyl methyl ether (**135**) and tin(IV) chloride. Distillation of the product mixture under reduced pressure (69-74 °C, 1.0 mm Hg) afforded 3-chloromethyl-2,5-dichlorothiophene (**138**) in 56% yield. Treatment of **138** with sodium hydride and diethyl malonate afforded the 2-((2,5-dichlorothiophen-3-yl)methyl)malonate (**140**) which was purified by distillation of the product mixture under reduced pressure (155-160 ºC 1.0 mm Hg) and was obtained as a colorless liquid in 75% yield. Saponification of the malonic ester **140** afforded the 2-((2,5-dichlorothiophen-3-

yl)methyl)malonic acid (**141**) as white solid in 90% yield. The malonic acid **141** was decarboxylated by distillation under reduced pressure (135-140 °C, 1.0 mm Hg) and the 3-(2,5-dichlorothiophen-3-yl)propanoic acid (**142**) was obtained in 86% yield. The resulted propionic acid **142** was converted to the 3-(2,5-dichlorothiophen-3-yl)propanoyl chloride (**133**) which was subjected to Friedel-Craft cyclization using aluminum trichloride to afford the dichloroketone (**132**).



Scheme 28 Synthesis of 1,3-dichloro-5,6-dihydrocyclopenta[*c*]thiophen-4-one (**132**)

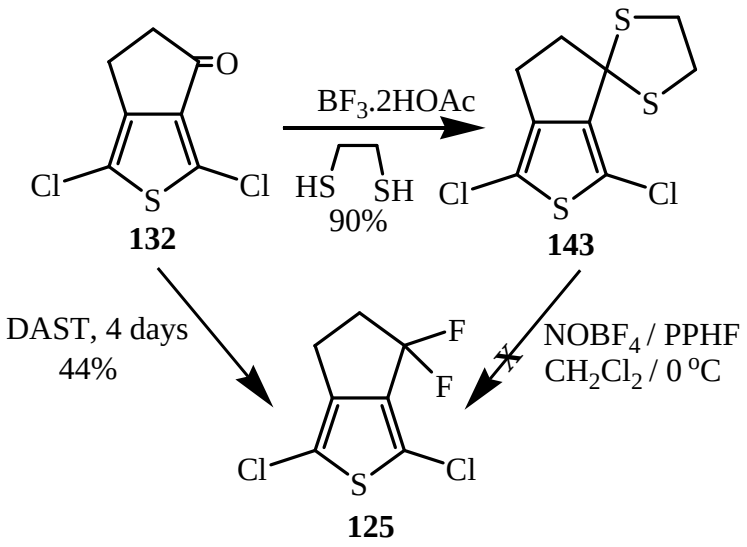
There are two factors should be taken into consideration when dealing with the Friedel-Craft cyclization reaction in the preparation of **132**. First: it is extremely important to distill the acid chloride **133** prior to the cyclization reaction, the use of non distilled acid chloride **133** led to a very poor yield of only 5%. Second: after the slow addition of the acid chloride at 0 °C, the reaction should be performed at room temperature to reduce the amount of the side product (compound **134**) to less than 5 % based on the ^{1}H NMR spectrum integration. Heating the reaction mixture under reflux led to the formation of a considerable amount of the cyclization at the 2-position (compound **134**) which was obtained in 20% yield based on the ^{1}H NMR spectrum integration and was identified by the presence of an aromatic ^{1}H NMR spectrum peak at 6.95 ppm. It was very difficult to separate **132** and **134**.

The next stage in our approach is the synthesis of 1,3-dichloro-4,4-difluoro-5,6-dihydrocyclopenta[*c*]thiophene (**125**) which is shown in Scheme 29. The attempted desulfurative fluorination of the 1,3-dithiolane **143** using the $NOBF_4$/PPHF afforded a mixture of inseparable products. On the other hand, the treatment of the dichloroketone **132** afforded the desired product **125** in moderate yield.

Spiro[1,3-dithiolane-2,4'-1',3'-dichloro-5',6'-dihydro-cyclopenta[*c*]thiophene (**143**) was prepared from the dichloroketone **132** in the same manner as the 1,3-dithiolane **76**. The attempt to synthesize the 1,3-dichloro-4,4-difluoro-5,6-dihydrocyclopenta[*c*]thiophene (**125**) by treating the spiro[1,3-dithiolane-2,4'-1',3'-dichloro-5',6'-dihydro-cyclopenta[*c*]thiophene (**143**) with pyridine polyhydrogen fluoride and nitrosonium tetrafluoroborate in dichloromethane led to the formation of the several

inseparable products based on the TLC experiment which showed at least ten separate spots.

Direct fluorination of the ketone **132** using a large excess of neat DAST ((diethyl amino)sulfur trifluoride) as a fluorinating reagent at 40-50 °C for four days afforded product **125** in 44% yield. The crude product was subjected to rapid filtration through short silica gel plug using diethyl ether as an eluant and the product was further purified by distillation. It is necessary to distill the product to remove the DAST impurities. It is worth noting that similar to the other fluorinated compounds, **125** undergoes some kind of decomposition as it is changed from colorless to dark solution upon storage. It is also a volatile compound and should be stored at low temperature.

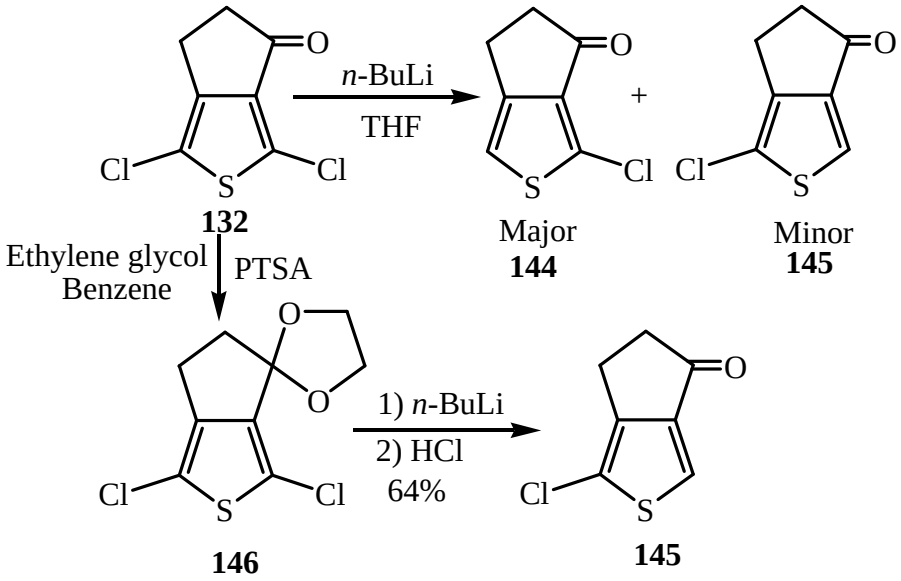


Scheme 29 Synthesis of 1,3-dichloro-4,4-difluoro-5,6-dihydrocyclopenta[*c*]thiophene (**125**)

4.3 Synthesis of the monomers and the dimers

The following target is to dechlorinate the thiophene ring selectively at the 2- and 5-position as shown in Scheme 30. This is a crucial step toward the preparation of the

dimers since it is essential to functionalize of thiophene ring prior to the coupling reactions. The mono-dechlorination was pursued because several attempts to reproduce the reported di-dechlorination using zinc, water and acetic acid failed.[134] Later on the di-dechlorination reaction was successfully performed and will be discussed separately.

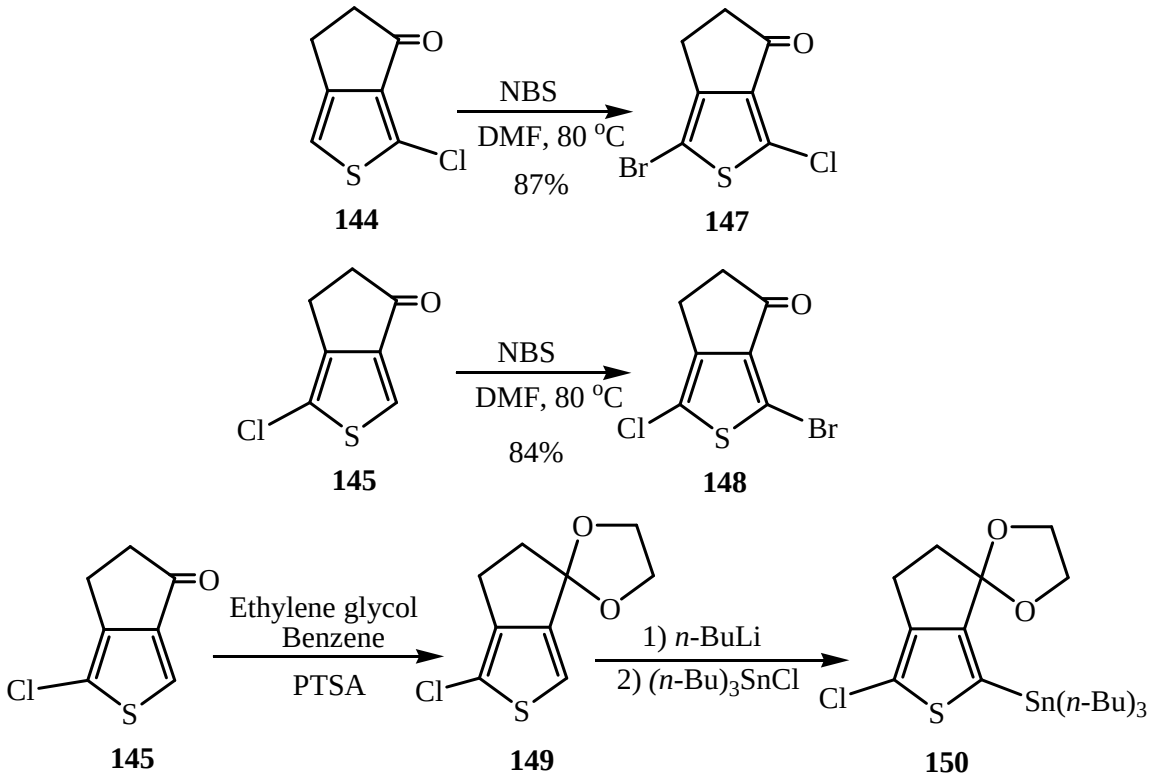


Scheme 30 Selective dechlorination of the thiophene ring

The treatment of 1,3-dichloro-5,6-dihydrocyclopenta[*c*]thiophen-4-one (**132**) with *n*-butyllithium at -78 °C followed by warming to room temperature led to the formation of both mono-chloro isomers 3-chloro-5,6-dihydrocyclopenta[*c*]thiophen-4-one (**144**) and 1-chloro-5,6-dihydrocyclopenta[*c*]thiophen-4-one (**145**). Isomer **144** was the major product and was obtained in 42% yield while isomer **145** was obtained in 17%. Converting the carbonyl group to the dioxalane **140** and treating it with *n*-butyllithium at -78°C followed by warming to -50°C led to the formation of only 1-chloro-5,6-dihydrocyclopenta[*c*]thiophen-4-one (**145**) in 64 % yield. The ^{1}H NMR spectrum of **144** was interesting as it showed a triplet at δ 6.78 ppm (J = 1.5 Hz) for the thiophene proton.

This results from the long range coupling between the thiophene proton and CH_2 protons of the cyclopentyl group. The ^1H NMR spectrum of **145** showed a singlet at δ 7.6 ppm for the thiophene proton since long range coupling is absent.

The functionalization of the thiophene ring is shown in Scheme 31. These are the key steps in the synthetic toward the preparation of the dimers.



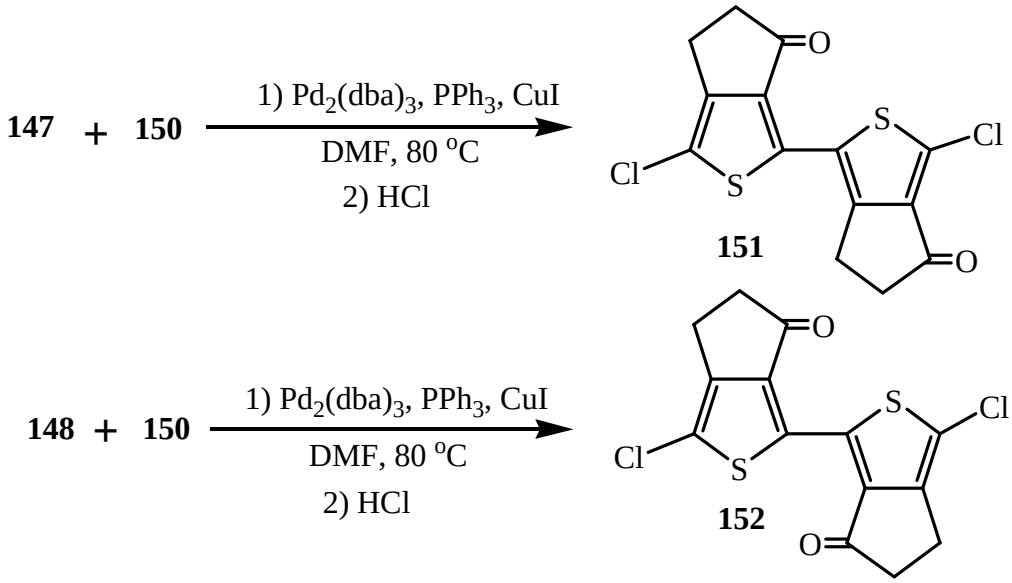
Scheme 31 Synthesis of the monomers

1-bromo-3-chloro-5,6-dihydrocyclopenta[*c*]thiophen-4-one (**147**) was prepared in 87% yield by the bromination of **144** using NBS (1.5 eq.) in DMF at 85 °C. 3-bromo-1-chloro-5,6-dihydrocyclopenta[*c*]thiophen-4-one (**148**) also was prepared in the same manner as **145**. The use of excess of NBS (1.5 equivalents) led to a significant improvent

in the reaction yield over the previous bromination reactions. In these particular reactions the bromine can only react at the desired position since the other locations are blocked.

Spiro[1,3-dioxalane-2,4'-1'-chloro-3'-tri-*n*-butylstannyl-5',6'-dihydro-cyclopenta[*c*]thiophene (**149**) was prepared from the ketal **150** similar to the preparation of **80**.

The diketone dimers were synthesized as shown in Scheme 32 by the Stille coupling reactions similar to the coupling reactions reported earlier.

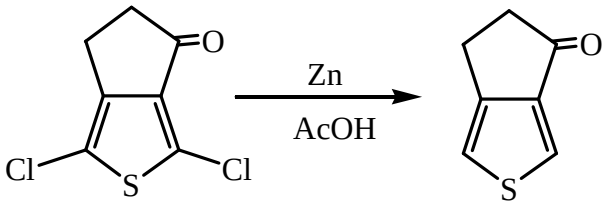


Scheme 32 Synthesis of the diketone dimers **150** and **151**

3,3'-dichloro-4,4',5,5'-tetrahydro-1,1'-bi(cyclopenta[*c*]thiophene)-4,6'-dione (**151**) and 3,3'-dichloro-4,4',5,5'-tetrahydro-1,1'-bi(cyclopenta[*c*]thiophene)-6,6'-dione (**152**) were synthesized using the Stille coupling reaction. It was very difficult to obtain pure samples from any of those molecules since they both showed very poor solubility in most organic solvents. The mass spectra showed that both compounds were formed (M^+ peaks at 342.2) but we were not able to obtain pure samples. After several attempts single

crystals (supposedly the desired dimers) were generated from the slow evaporation of the THF solution. Attempts to obtain X-ray crystal structures on both dimers failed. Twined crystals were obtained for the H-T isomer **151** and small crystals were obtained for the H-H isomer **152**. The x-ray crystal structures are not resolved at this time.

Another approach was pursued in an attempt to solve the previous problems. In this approach after several attempts both chlorine atoms were removed successfully. 5,6-Dihydrocyclopenta[*c*]thiophen-4-one (**126**) synthesized as shown in Scheme 33.



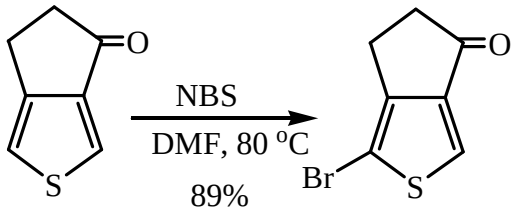
132 **126**

Scheme 33 Synthesis of 5,6-dihydrocyclopenta[*c*]thiophen-4-one (**126**)

The ideal components of the dechlorination reaction are the use of zinc (30 mesh granules) and glacial acetic acid (5%). The product **126** was obtained in a low yield of 15%. This low yield is attributed to complexity of this reaction. The major product of this reaction is the mono-dechlorination at the 3- (major: **145**) and the 1-position (minor: **144**) in addition to several other products. Running the reaction for extended periods of time led to the formation of an inseparable mixture of products possibly including the polymeric material. Reports in the literature supported these findings in which this reaction led to the formation of the desired product **126** in 30% yield in addition to **145** in 45% yield and the polymeric material in 25%.[137,138] Performing the reaction using zinc powder and/or >10% of glacial acetic acid led to the formation of an inseparable mixture

of products while performing the reaction without the use of glacial acetic acid led to the formation of only **145**.

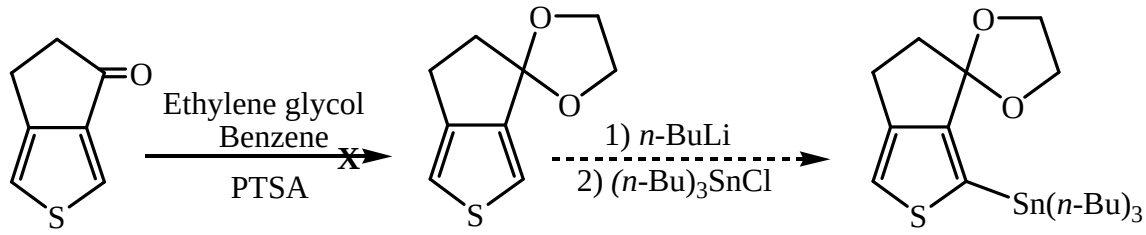
The next step is to employ the same set of Stille coupling reactions done previously to prepare the dimers or the trimers. The typical bromination reaction was used on 5,6-dihydrocyclopenta[*c*]thiophen-4-one (**126**) and this led to the formation of 1-bromo-5,6-dihydrocyclopenta[*c*]thiophen-4-one (**153**) in 89% yield as shown in Scheme 34.



126 **153**

Scheme 34 Preparation of 1-bromo-5,6-dihydrocyclopenta[*c*]thiophen-4-one (**153**)

The attempt to prepare spiro[1,3-dioxalane-2,4'-5',6'-dihydro-cyclopenta[*c*]thiophene (**153**) failed and a black material (possibly the polymerized material) was obtained from the reaction.



126 **154** **155**

Scheme 35 Attempted synthesis of spiro[1,3-dioxalane-2,4'-5',6'-dihydro-cyclopenta[*c*]thiophene (**153**)

4.4 Conclusion

In this chapter we showed significant progress toward the synthesis of fluorinated fused five-membered ring systems. The synthesis of the H-T 3,3'-dichloro-4,4',5,5'-tetrahydro-1,1'-bi(cyclopenta[*c*]thiophene)-4,6'-dione (**151**) and H-H 3,3'-dichloro-4,4',5,5'-tetrahydro-1,1'-bi(cyclopenta[*c*]thiophene)-6,6'-dione (**152**) dimers were accomplished, although the isolation and purification of those dimers was very difficult. Crystals that could be the dimers were obtained. Unfortunately we were not able to obtain the x-ray crystal structures.

CHAPTER 5

EXPERIMENTAL

5.1 General procedures

All reactions were carried out in dried glassware. All solvents were dried over 3A molecular sieves. Anhydrous DMSO (>99.9%) was obtained in Sure/Seal™ bottles from Aldrich Chemical Co. Fresh copper powder was prepared by the literature method.[110] Flash chromatography was performed using flash silica gel 32-63µm, 60 Å.

^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on a JEOL Eclipse 500 NMR spectrometer (unless reported otherwise) at 500.16 MHz, 125.76 MHz and 470.62 MHz, respectively, using $CDCl_3$ solvent with tetramethylsilane as an internal standard for ^{1}H, residual $CHCl_3$ for ^{13}C and $CFCl_3$ for ^{19}F NMR spectra. Data are reported as follows: chemical shifts in ppm (δ), multiplicity (singlet = s, doublet = d, triplet = t, quartet = q, quintet = p, multiplet = m, broad singlet = bs), coupling constants in Hz, (* in the appendix indicates spinning side bands). It is worth noting that ^{1}H NMR showed that there is a coupling between the thiophene protons and the Sn (I = 0) which will not be reported.

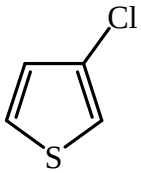
FT-IR spectra were obtained on a Biorad-Digilab FTS-40 Fourier Transform Infrared using powdered samples (approximately 1-2% sample weight) with KBr in a diffuse reflectance unit or liquid samples between KBr plates.

Elemental analyses were performed using a Perkin Elmer Series II CHN analyzer. Melting points were determined using a Thomas-Hoovver capillary melting point apparatus and were uncorrected.

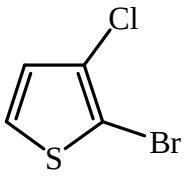
70 eV electron impact mass spectra were obtained on a Bear Kodiak 1200 Triple Quad Spectrophotometer. High resolution mass spectra (HR-EIMS) were done at the University of Florida.

X-ray structure determination. A suitable crystal covered with a layer of cold hydrocarbon oil was selected and mounted with paratone-N oil in a cryo-loop and immediately placed in the low-temperature nitrogen stream. The X-ray intensity data were measured at 100(2) K on a Bruker SMART APEX CCD area detector system equipped with a Oxford Cryosystems 700 Series cooler, a graphite monochromator, and a Mo K_α fine-focus sealed tube ($\lambda \doteq 0.710\ 73$ Å). The data frames were integrated with the Bruker SAINT-Plus software package. Data were corrected for absorption effects using the multi-scan technique (SADABS). Structures were solved and refined using Bruker SHELXTL (Version 6.14) software package. All the non hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at calculated positions.

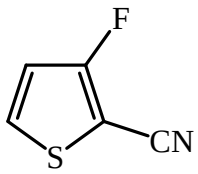
3-Chlorothiophene (**41**).[89] A well stirred mixture of 3-bromothiophene (**50**) (50 g, 0.30 mol) and anhydrous copper(I) chloride (60 g, 0.60 mol) in dry DMF (dimethylformamide; 200 mL) was heated for 24 hours under reflux under a nitrogen atmosphere. After the reaction mixture was cooled, water (500 mL) was added. A Dean-Stark trap was attached and 3-chlorothiophene (**41**) was codistilled with water. The organic layer was separated and dried over calcium chloride. 3-Chlorothiophene (**41**) was further purified by vacuum distillation, bp: 22-25 ºC / 0.1 mm Hg to give 32.6 g, 89% yield, b.p. 135-138 ºC, (lit.[89] 137-139 ºC). ^{1}H NMR ($CDCl_3$) δ 7.24 (dd, *J* =5.0 Hz, *J* = 3.3 Hz, 1H), δ 7.08 (dd, *J* = 3.3 Hz, *J* = 1.3 Hz, 1H), δ 6.94 (dd, *J* = 5.0 Hz, *J* = 1.3 Hz, 1H), [Lit.[139] (CCl_4) δ 6.85 (d, *J* = 4.8 Hz), δ 6.98 (d, *J* = 1.5 Hz), δ 7.17 (d, *J* = 3.2 Hz)]. ^{13}C NMR ($CDCl_3$) δ 127.6, 126.0, 125.5, 119.8.



2-Bromo-3-chlorothiophene (**51**).[90] A solution of 3-chlorothiophene (**41**), (26.5 g, 0.22 mol) and NBS (*N*-bromosuccinimide) (53.4 g, 0.30 mol) was prepared in chloroform (150 mL) and acetic acid (150 mL). The reaction mixture was heated under reflux for 2 hours. After being cooled, the mixture was poured into water (500 mL) and the organic layer was separated, washed with dilute KOH solution and water until the solution was clear, then dried over $MgSO_4$. The solvent was removed by rotary evaporation. The product **51** was purified by distillation through a 10 cm Vigreux column under vacuum, bp: 55-60 ºC / 0.1 mm Hg to give 31.4 g, 72% yield, b.p. 195-198 ºC / 760 mm Hg, (lit.[90] 194 ºC / 760 mm Hg). ^{1}H NMR ($CDCl_3$) δ 7.22 (d, *J* = 5.7 Hz, 1H), δ 6.85 (d, *J* = 5.7 Hz, 1H), [Lit.[90] ^{1}H NMR (neat liquid) δ 7.22 (d, *J* = 5.8 Hz), δ 6.85 (d, *J* = 5.7 Hz)]. ^{13}C NMR ($CDCl_3$) δ 127.6, 127.1, 125.9, 108.6.

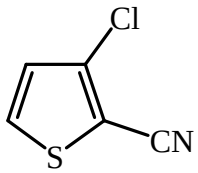


3-Chloro-2-cyanothiophene (50).[88] To a solution of 2-bromo-3-chlorothiophene (**51**)



(29.0 g, 0.147 mol) in anhydrous DMF (100 mL) was added copper(I) cyanide (17.5 g, 0.195 mol). The solution was stirred under nitrogen and refluxed for 5 hours. The mixture was cooled to 100 ºC. $FeCl_3 \cdot 6H_2O$ (60 g, 0.22 mol) was dissolved in water (100 mL) containing concentrated HCl (25 mL) and this was added to the reaction mixture which was then refluxed for an additional 30 minutes. After being cooled, the mixture was extracted with dichloromethane (6 x 100 mL) then washed with water (3 x 50 mL), with 6N HCl (2 x 50 mL), and with saturated sodium bicarbonate solution (2 x 50 mL), then dried over magnesium sulfate. The solvent was removed by rotary evaporation. 16.2 g, 77% yield of the product was collected as a pale yellow solid. mp 60-62 °C, [lit.[88] 62 °C]. ^{1}H NMR ($CDCl_3$) δ 7.58 (d, *J* = 5.3 Hz, 1H), δ 7.05 (d, *J* = 5.3 Hz, 1H). [Lit.[88] ^{1}H NMR: ($CDCl_3$) δ 7.59 (d, *J* = 5.3 Hz), δ 7.06 (d, *J* = 5.4 Hz)]. ^{13}C NMR ($CDCl_3$) δ 136.3, 132.2, 128.3, 111.9, 106.2.

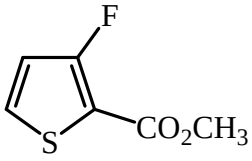
Attempted preparation of 3-flouro-2-cyanothiophene (52).[88] 3-Chloro-2-



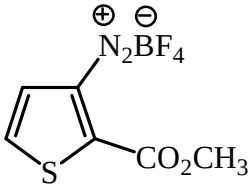
cyanothiophene (**50**), 2.15 g (0.015mol), was dissolved in DMSO (40 mL) and CsF, 4.0 g (0.026 mol), was added to the solution. The mixture was refluxed for 24 hours. After cooling, the reaction mixture was diluted with 100 mL of CH_2Cl_2**.** Charcoal was added to the mixture and then the mixture was stirred for 20 minutes and filtered. The solution was washed repeatedly with water, and saturated sodium bicarbonate then dried over $MgSO_4$. The solvent was removed by rotary evaporator to produce white solid, 0.7 g. TLC showed this to be a

mixture of many inseparable compounds. ^{19}F NMR ($CDCl_3$) ($CFCl_3$) δ -119.01 (d, J = 4.6 Hz), δ -119.03 (d, J = 4.6 Hz).

2-Methoxycarbonylthiophene-3-diazonium tetrafluoroborate (47).[82] Methyl 3-aminothiophene-2-carboxylate (**44**), 9.4 g (0.60 mol), was added gradually to 25 mL of a vigorously stirred 6M hydrochloric acid solution. The reaction mixture was stirred for 30 min at room temperature and then cooled to below 0 °C (ice-salt bath). 4.20 g (0.60 mol) of sodium nitrite was dissolved in 10 mL of water and was added to the mixture which was stirred for 1 hour at that temperature. Tetrafluoroboric acid (65%) solution (20 mL) was added dropwise. The white powder product which precipitated was filtered, rinsed with hot ethanol (30 mL) and dried under vacuum. 14.4 g (93% yield) was collected, mp 140-143 °C, [lit.[82] 142-143 °C].

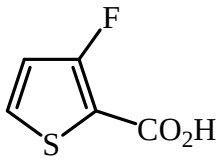


Methyl 3-fluorothiophene-2-carboxylate (45).[83] A mixture of 2-methoxycarbonylthiophene-3-diazonium tetrafluoroborate (**47**), 15.4 g (0.060, mol) and 80.0 g of sand in a round-bottomed flask was attached to a distilling head connected to another round-bottomed flask and a Dewar type condenser cooled with liquid nitrogen. The mixture was heated and when the temperature reached 160 °C (oil-bath temperature) under vacuum (0.1 mm Hg), the product **45** sublimed and was trapped on the inner surface of the condenser, then at ca. 200 °C a pale yellow liquid distilled and solidified in the round bottomed flask. The product inside the condenser and the round bottomed flask were combined and washed repeatedly with methanol until it all dissolved. The product **55** was



collected as a pale yellow solid upon the addition of water. The product was filtered and air dried, 6.4 g was collected, 67% yield. mp 48-50 °C (lit.[83] 51-53 °C). ^{1}H NMR ($CDCl_3$) δ 7.42 (dd, J = 5.5 Hz, J_{H-F} = 3.8 Hz, 1H), δ 6.86 (d, J = 5.5 Hz, 1H), δ 3.89 (s, 3H), [Lit.[83] ^{1}H NMR ($CDCl_3$) δ 7.42 (dd, J = 5.5 Hz, J = 3.8 Hz, 1H), δ 6.85 (dd, J = 5.5 Hz, J = 0.5 Hz, 1H), δ 3.89 (s, 3H)]. ^{13}C NMR ($CDCl_3$) δ 160.9 (d, J_{C-F} = 3.8 Hz), 160.2 (d, $^{1}J_{C-F}$ = 276.4 Hz) 130.1 (d, J_{C-F} = 10.5 Hz), 118.5 (d, J_{C-F} = 24.9 Hz), 112.5 (d, J_{C-F} = 10.1 Hz), 51.9 (s), [Lit.[83] ^{13}C NMR ($CDCl_3$) δ 161.8 (C-3), 130.0 (C=O), 129.9 (C-5), 118.5 (C-4), 118.1 (C-2), 51.9 (OCH_3)]. ^{19}F NMR ($CDCl_3$) ($CFCl_3$) (H-coupled) δ – 115.4 (d, J = 3.5 Hz), [Lit.[83] ^{19}F NMR ($CDCl_3$) ($CFCl_3$) δ – 115.4 (d, J = 3.7 Hz)]. Anal. Calcd. for $C_6H_5FO_2S$: C 44.99; H 3.15. Found: C 44.75; H 3.00.

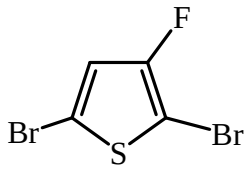
3-Fluorothiophene-2-carboxylic acid (48).[82] To a stirred solution of methyl 3-fluorothiophene-2-carboxylate (**45**), 12.0 g (0.072 mol), in 50 mL of ethanol, 50 mL of 1M sodium hydroxide was added. The reaction mixture was refluxed for 1 hour. The solvent was removed with a rotary evaporator and the residue was then dissolved in 250 mL of water and acidified with a 10% hydrochloric acid (v/v) solution. The white solid product that formed was filtered, washed with water, and rinsed with hot hexane. The cooled hexane was decanted and the product was air dried. 8.85 g was collected, 84% yield, mp 165-168 °C (dec.), (Lit.[88] 158 °C) (Lit.[87] 172-173 °C). ^{1}H NMR ($CDCl_3$) δ 10.7 (bs, 1H), δ 7.52 (dd, J = 5.5 Hz, J_{H-F} = 3.8 Hz, 1H), δ 6.85 (d, J = 5.5 Hz, 1H), [lit.[14] ^{1}H NMR ($CDCl_3$) δ 10.7 (s), δ 7.53 (dd, J = 5.5 Hz, J = 3.6 Hz), δ 6.90 (d, J = 5.4 Hz)], [Lit.[88] ^{1}H NMR ($CDCl_3$) δ 7.85 (dd, J = 5.5 Hz, J = 4.2 Hz), δ 7.12 (dd, J = 5.4 Hz)]. ^{13}C NMR ($CDCl_3$) δ



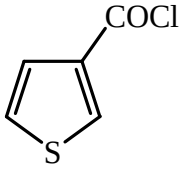
166.0 (d, $^{3}J_{C\text{-}F}$ = 2.6 Hz), 161.4 (d, $^{1}J_{C\text{-}F}$ = 279.0 Hz) 131.8 (d, *J* = 10.1 Hz), 118.7 (d, *J* = 24.7 Hz), 111.9 (d, *J* = 10.1 Hz), [Lit.[88] ^{13}C NMR ($CDCl_3$) δ 161.94, 158.96(d, *J* = 245.7 Hz), 131.43 (d, *J* = 10.5 Hz), 118.81 (d, *J* = 22.5 Hz), 113.41 (d, *J* = 10.3 Hz)]. ^{19}F NMR ($CDCl_3$) ($CFCl_3$) δ −112.6 (d, *J* = 3.5 Hz). [Lit.[88] ^{19}F NMR ($CDCl_3$) ($CFCl_3$) δ −115.98 (d, *J* = 4.1 Hz)].

3-Fluorothiophene (22). The decarboxylation of 3-fluorothiophene-2-carboxylic acid (**48**) was carried out similar to a reported thiophene decarboxylation.[91] 3-Fluorothiophene-2-carboxylic acid (**48**), 1.68 g (80 mmol) was dissolved in 10 mL of quinoline in a one-necked round-bottomed flask connected to a distillation apparatus. 1.24 g (40 mmol) of barium promoted copper chromite was added to the solution and the temperature was raised to 200 °C (oil-bath). The product (highly volatile) was distilled at 30-32 °C (distilling head thermometer) and collected in a cold receiver (ice-bath). 0.80 g was collected, 93% yield. ^{1}H NMR ($CDCl_3$) δ 7.17 (dt, *J* = 5.4 Hz, *J* = 3.4 Hz, 1H), δ 6.83 (ddd, *J* = 5.4 Hz, *J* = 1.5 Hz, *J* = 0.9 Hz, 1H) δ 6.69 (ddd, *J* = 3.4 Hz, *J* = 1.5 Hz, *J* = 1.1 Hz, 1H), [Lit.[88] ^{1}H NMR ($CDCl_3$) δ 7.15 (ddd, *J* = 5.4 Hz, *J* = 3.4 Hz, *J* = 3.4 Hz, 1H), δ 6.85 (ddd, *J* = 5.5 Hz, *J* = 2.4 Hz, *J* = 1.1 Hz, 1H) δ 6.7 (ddd, *J* = 3.4 Hz, *J* = 2.4 Hz, *J* = 1.1 Hz, 1H)]. ^{13}C NMR ($CDCl_3$) δ 158.5 (d, $^{1}J_{C\text{-}F}$ = 257.7 Hz), 124.8(d, $J_{C\text{-}F}$ = 9.1 Hz) 117.2 (d, $J_{C\text{-}F}$ = 26.9 Hz), 103.1 (d, $J_{C\text{-}F}$ = 21.1 Hz), [Lit.[88] ^{13}C NMR ($CDCl_3$) δ 158.5 (d, *J* = 257.5 Hz), 124.8 (d, *J* = 9.2 Hz) 117.3 (d, *J* = 26.9 Hz), 103.2 (d, *J* = 21.1 Hz)]. ^{19}F NMR ($CDCl_3$) ($CFCl_3$) δ −131.0 (d, *J* = 2.3 Hz), [Lit.[88] ^{19}F NMR ($CDCl_3$) ($CFCl_3$) δ −131.0 (d, *J* = 3.2 Hz)].

2,5-Dibromo-3-fluorothiophene (38).[93] Into a dry 250 mL three-necked round bottomed flask fitted with a reflux condenser were placed 1.46 g (0.010 mol) of 3-fluorothiophene-2-carboxylic acid (**48**), 3.24 g (0.015 mol) of red mercuric oxide and 100 mL of carbon tetrachloride. While the flask was being irradiated with an adjacent 150-W bulb, 3.16 g (0.020 mol) of bromine was added slowly via a syringe. The reaction mixture was irradiated for thee hours and cooled to room temperature. Saturated $NaHCO_3$ (30 mL) was added and the mixture was vigorously stirred for 15 min. The mixture was vacuum filtered through a celite pad and the pad was washed with chloroform (3 x 20 mL). The organic phase was washed with $NaHCO_3$ (3 x 20 mL), NaCl (3 x 20 mL) and dried over $MgSO_4$. The solvent was removed by rotary evaporation. The product **38** was purified using fractional distillation column at 120 ºC (oil-bath) (100 mm, Claisen-Vigreux column with condenser) under vacuum (bp: 54-56 ºC / 0.01 mm Hg). 1.72 g was collected (66% yield). ^{1}H NMR ($CDCl_3$) δ 6.79 (d, *J* = 1.2 Hz) [lit.[92] ^{1}H NMR (CCl_4) δ 6.79 (d, *J* = 1.3 Hz)]. ^{13}C NMR ($CDCl_3$) δ 154.7 (d, *J* = 263.9 Hz), 120.5 (d, *J* = 26.1 Hz) 110.4 (d, *J* = 12.0 Hz), 90.6 (d, *J* = 22.6 Hz). ^{19}F NMR ($CDCl_3$) ($CFCl_3$) δ – 124.0.

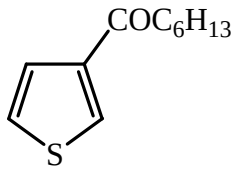


3-Thenoyl Chloride (61).[97] Thiophene-3-carboxylic acid (**62**) (12.8 g, 0.100 mol) and $SOCl_2$ (60 mL) were placed in a 100 mL one-necked flask, and then 2 drops of DMF was added. The mixture was refluxed for 6 hours. After the excess $SOCl_2$ was removed by simple distillation, the product was recrystallized from 15 mL of diethyl ether. After decanting the ether and vacuum drying, 3-thenoyl chloride (**61**) (13.6 g, 92% yield) was collected as colorless crystals, mp 50-52



°C (lit.[98] 50-51 °C). ^{1}H NMR ($CDCl_3$) δ 8.37 (dd, *J* = 3.0 Hz, *J* = 1.3 Hz), δ 7.57 (dd, *J* = 5.2 Hz, *J* = 1.3 Hz), δ 7.39 (dd, *J* = 5.2 Hz, *J* = 3.0 Hz).

3-Heptanoylthiophene (60).[97] The Grignard reagent was prepared by standard methods,



that is: Mg turnings (2.0 g, 0.082 g-atom) and dry THF (60 mL) were put into a 250 mL three-necked flask equipped with a stirring bar, an addition funnel, an inlet for dry argon, and a condenser with a drying tube. Next, 1-bromohexane (12.38 g, 0.075 mol) in dry THF (150 mL) was added to the flask dropwise over 2 hours. The mixture was refluxed for 2 hours, cooled to room temperature, and used in the next step.

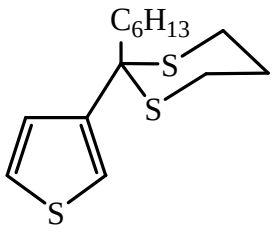
12.46 g (0.085 mol) of 3-thenoyl chloride (**61**) (12.46 g, 0.085 mol) was dissolved in dry THF (100 mL) in a 500 mL three-necked flask equipped with a stirring bar, an addition funnel and an inlet for dry argon. The Grignard solution was transferred to the addition funnel through a long double-tipped cannula. The flask was cooled to -78 °C (acetone-Dry Ice) and the Grignard reagent was added to the solution via the addition funnel dropwise over 7 hours. The solution was brought to room temperature over 3 hours and the mixture was poured into 400 mL of water. The aqueous phase was washed with ether (4 x 100 mL), the combined organic phase was washed with 1 M NaOH (3 x 100 mL), sat. NaCl solution (3 x 100 mL), and water (3 x 100 mL) and then dried over $MgSO_4$. The solvent was removed with a rotary evaporator. 10.9 g of the crude mixture was obtained and was subjected to flash chromatography (hexane:ether = 95:5). 3-heptanoylthiophene (**60**) (6.2 g, 46% yield) was collected as a pale yellow oil. ^{1}H NMR ($CDCl_3$) δ 8.03 (dd, *J* = 3.0, *J* = 1.0 Hz, 1H), δ 7.54 (dd, *J* = 5.0, *J* = 1.0 Hz, 1H), δ 7.29

(dd, *J* = 5.0, *J* = 3.0 Hz, 1H), δ 2.86 (t, *J* = 7.0 Hz, 2H), δ 1.71 (p, *J* = 7.0 Hz, 2H), δ 1.26-1.38 (bm, 6H), δ 0.88 (m, 3H). [Lit.[97] ^{1}H NMR ($CDCl_3$) δ 8.04 (d, *J* = 3 .0 Hz), δ 7.55 (d, *J* = 5), δ 7.31 (dd, *J* = 6.0 Hz, *J* = 3.0 Hz), δ 2.87 (t, *J* = 7.0 Hz), δ 1.72 (p, *J* = 7.0 Hz), δ 1.26-1.42 (m), δ 0.89 (t, *J* = 7.0 Hz)]. ^{13}C NMR: ($CDCl_3$) (^{1}H decoupled) δ 194.9, 142.5, 131.6, 127.0, 126.2, 39.9, 31.7, 29.0, 24.4, 22.5, 14.0. [Lit.[97] ^{13}C NMR: ($CDCl_3$) (^{1}H decoupled) δ 195.0, 142.4, 131.7, 127.0, 126.2, 39.9, 31.6, 29.0, 24.4, 22.5, 14.0].

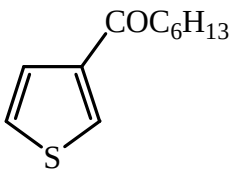
2-Thiophene-3-yl-(1,3)dithiane (70). Thiophene-3-carboxaldehyde (**69**) (11.2 g, 0.10 mol, 1.0 eq) was dissolved in THF (50 mL). To this solution 1,3-propanedithiol (15.0 mL, 1.5 mol, 1.5 eq) and Amberlyst-15 resin (5.00 g) were added. The reaction was vigorously stirred overnight, then filtered and washed with ethyl acetate (3 x 150 mL). The filtrate was extracted with saturated aqueous Na_2CO_3 solution (2 x 150 mL) followed by brine (2 x 150 mL), and was then dried over $MgSO_4$, filtered, and the solvent was removed by rotary evaporation. The product purified by flash chromatography ethyl acetate:hexane (2:10). The dithiane **70** was obtained in 88% yield (17.8 g) was collected as white crystals, mp 79-80 °C. ^{1}H NMR ($CDCl_3$) δ 7.36 (ddd, *J* = 3.0, *J* = 1.3, *J* = 0.7 Hz, 1H), 7.27 (dd, *J* = 5.0, *J* = 3.0 Hz, 1H) 7.17 (dd, *J* = 5.0, *J* = 1.3 Hz, 1H), 5.29 (s, 1H), 3.00 (m, 2H), 2.89 (m, 2H), 2.15 (m, 1H), 1.92 (m, 1H). ^{13}C NMR: ($CDCl_3$) (^{1}H decoupled) δ 139.4, 127.0, 125.9, 123.1, 45.7, 31.5, 25.2. IR (KBr, cm^{-1}) 3104, 3077, 3036, 2936, 2897, 2825, 1764, 1573, 15026, 1506, 1416, 1299, 1276, 1178, 1079, 1009,

953, 908, 862, 836, 802, 752, 694, 677. Anal. Calcd. for $C_8H_{10}S_3$: C 47.48; H 4.98. Found: C 47.08; H 4.99

2-Hexyl-2-thiophene-3-yl-(1,3)dithiane (71). A solution of 2-thiophene-3-yl-(1,3)dithiane (**70**). (2.02 g, 10.0 mmol) in anhydrous THF (70.0 mL) was treated under argon at -78 °C with *n*-butyllithium (10.0 mL, 1.6 M, 16.0 mmol). After stirring for 1 h at -78 °C, a solution of 1-bomohexane (2.48 g, 15.0 mmol) in dry THF (10 mL) was added. This reaction mixture was stirred at -78 °C for 2 h and allowed to warm to room temperature over 6 hours. The mixture was poured into 100 mL of H_2O and was extracted with EtOAc (3 x 100 mL). The combined organic layers were dried over $MgSO_4$ and concentrated by rotary evaporation. The product was subjected to flash chromatography, hexane/ EtOAc (5:1) to give **5** (2.1 g, 73%) as a colorless oil. ^{1}H NMR ($CDCl_3$) 7.36 (dd, *J* = 3.0, *J* = 1.0 Hz, 1H), 7.29 (dd, *J* = 5.0, *J* = 3.0 Hz, 1H), 7.25 (dd, *J* = 5.0, *J* = 1.3 Hz, 1H), 2.79 (m, 2H), 2.68 (m, 2H), 1.97 (m, 4H), 2.0-185 (bm, 8H), 0.83 (t, *J* = 7.0, 3H). ^{13}C NMR: ($CDCl_3$) (^{1}H decoupled) δ144.7, 128.5, 125.8, 124.7, 55.5, 44.5, 31.6, 29.3, 27.8, 25.5, 23.9, 22.6, 14.1. IR (KBr, cm^{-1}) 3102, 2924, 2855, 1459, 1423, 1376, 1362, 1277, 1213, 907, 862, 836, 797, 778, 664. Anal. Calcd. for $C_{14}H_{22}S_3$: C 58.69; H 7.74. Found: C 58.39; H 8.02.



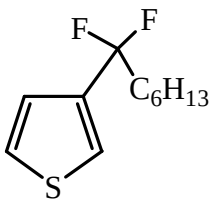
3-Heptanoylthiophene (60). To a solution of 2-hexyl-2-thiophene-3-yl-(1,3)dithiane (**71**) (4.01 g, 0.014 mol) and red mercuric oxide (6.06 g, 0.028 mol) in 15% aqueous THF (100 mL), was added dropwise boron trifluoride etherate (5.3 mL, 0.042 mol). The mixture was stirred



at room temperature for 16 hours, and then was diluted with 200 mL of ether. The mixture was filtered through a celite plug using a glass frit. The filtrate was washed with 5% aqueous $NaHCO_3$ (2 x 100 mL), water (2 x 100 mL) and then dried over $MgSO_4$. The solvent was removed by rotary evaporation. The crude mixture was obtained and subjected to flash chromatography, hexane:EtOAc (7:3). 3-Heptanoylthiophene (**60**) was obtained as a yellow oil (2.75g, 93% yield).

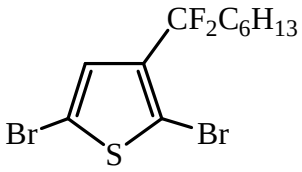
2-Hexyl-2-thiophen-3-yl-1,3-dithiolane (77). 3-Heptanoylthiophene (**60**) (1.50 g, 7.6 mmol) and 1,2-ethandithiol (1.5 mL,18 mmol) were combined under argon and stirred, followed by the addition boron trifluoride-acetic acid complex (1.2 mL, 8.6 mmol). The biphasic mixture was allowed to stir vigorously for 30 min. The mixture was diluted with hexane (20 mL), the organic layer was separated and washed with saturated $NaHCO_3$ (3 x 20 mL), 1M NaOH (2 x 20 mL), saturated NaCl (2 x 20 mL) and water (2 x 20 mL). The organic extract was dried over $MgSO_4$ and the solvent was removed by rotary evaporation. The mixture was subjected to flash chromatography using hexane:EtOAc (5:1). The product was collected as a colorless oil, (1.9 g, 89% yield). ^{1}H NMR ($CDCl_3$) δ 7.36 (dd, *J* = 3.0, *J* = 1.4 Hz, 1H), δ 7.26 (dd, *J* = 5.0, *J* = 3.0 Hz, 1H), δ 7.11 (dd, *J* = 5.0, *J* = 1.4 Hz, 1H), δ 3.38-3.25 (m, AA'BB', 4H) δ 2.30 (m, 2H), δ 1.20-1.40 (bm, 8H), δ 0.84 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR: ($CDCl_3$) (^{1}H decoupled) δ 147.3, 127.0, 126.0, 122.2, 70.2 44.9, 39.2, 31.6, 29.3, 27.8, 22.6, 14.0. IR (KBr, cm^{-1}) 3103, 2922, 2853, 1461, 1416, 1373, 1276, 1217, 837, 766, 649. HRMS (m / z): $[M + H]^+$ calcd for $C_{13}H_{21}S_3$, 273.0761; found, 273.0830.

3-(1,1-Difluoroheptyl)thiophene (72). The dithiolane **77** (1.0 g, 4.0 mmol) dissolved in



5 mL of dichloromethane was added dropwise to a solution of (1.1 g, 9.0 mmol) $NO^+BF_4^-$ and 60% PPHF (pyridinium polyhydrogen fluoride) (5 mL) in dichloromethane (10 mL), in a 25 mL plastic bottle at 0 °C (ice-bath) under an argon atmosphere. The mixture was stirred at room temperature for one hour and the reaction mixture was transferred to a plastic graduated cylinder. The mixture was diluted with 50 mL of petroleum ether to form two layers. The top layer was separated from the bottom layer (the PPHF layer) and passed through a short column packed with Al_2O_3 (20 g) and $MgSO_4$ (10 g). The solvent was removed by rotary evaporation. The product was passed through a short silica plug (5 cm) (hexane:ether 95:5). The filtrate was concentrated by vacuum and the product **72** was collected (0.3 g, 40% yield). ^{1}H NMR ($CDCl_3$) δ 7.45 (m, 1H), δ 7.34 (m, 1H), δ 7.11 (dd, *J* = 5.0, *J* = 1.3 Hz, 1H), δ 2.17-2.08 (m, 2H,), δ 1.47-1.40 (bm, 2H), δ 1.34-1.23 (bm, 6H), δ 0.86 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR: ($CDCl_3$) (^{1}H decoupled) δ 139.2 (t, *J* = 30.0 Hz), 126.6, 125.0 (t, *J* = 4.0 Hz), 123.6 (t, *J* = 7.0 Hz), 121.6 (t, *J* = 241.5 Hz), 38.9 (t, *J* = 26.9 Hz), 31.6, 29.0, 22.6, 22.5, 14.1. ^{19}F NMR ($CDCl_3$) ($CFCl_3$) δ -90.4 (t, *J* = 17.2 Hz). HRMS (m / z): $[M + H]^+$ calcd for $C_{11}H_{17}F_2S$, 219.0974; found, 219.0988.

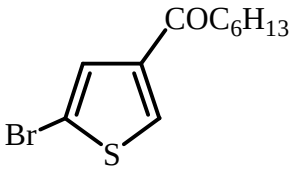
2,5-dibromo-3-(1,1-Difluoroheptyl)thiophene (73). DBH (1,3-dibromo-5,5-



dimethylhydantoin) (1.1 g, 9 mmol) in dichloromethane (10 mL) was placed in a 125 mL plastic bottle at -78 °C under argon atmosphere. To the suspension was added dropwise 60% PPHF (pyridinium polyhydrogen fluoride) (5 mL). The mixture was stirred for 30 min,

then dithiolane **77** (1.09 g, 0.40 mmol) dissolved in dichloromethane (5 mL) was added dropwise over 10 min. The reaction was warmed to room temperature over 6 hours. The reaction mixture was transferred to a plastic graduated cylinder. The mixture was diluted with 50 mL of petroleum ether to form two layers. The top layer was separated from bottom the PPHF layer and passed through a glass frit packed with Al_2O_3 (5 g) and $MgSO_4$ (1 g). The solvent was removed by rotary evaporation. The product was subjected to flash chromatography (100% hexane). The product **73** was collected as colorless oil (125 mg, 90% yield). ^{1}H NMR ($CDCl_3$) δ 6.97 (s, 1H), δ 2.22-2.12 (m, 2H, CF_2CH_2), δ 1.45-1.37 (bm, 2H), δ 1.34-1.23 (bm, 6H), δ 0.88 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR: ($CDCl_3$) (^{1}H decoupled) δ 138.4 (t, *J* = 31.2 Hz), 129.5 (t, *J* = 23.0 Hz), 120.8 (t, *J* = 242.8 Hz), 111.7, 109.7 (t, *J* = 7.0 Hz), 37.6 (t, *J* = 105.0 Hz), 31.6, 28.9, 22.4, 22.3 (t, *J* = 15.3 Hz), 14.0. ^{19}F NMR ($CDCl_3$) ($CFCl_3$) δ -91.4 (t, *J* = 16.6 Hz). IR (KBr, cm^{-1}) 3107, 2956, 2930, 2859, 1540, 1464, 1420, 1377, 1357, 1195, 1177, 1123, 1066, 968, 863, 730. HRMS (m / z): $[M]^+$ calcd for $C_{11}H_{14}Br_2F_2S$, 373.9131; found, 373.9177.

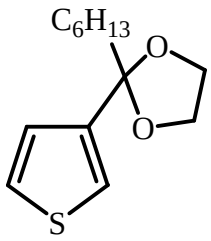
5-Bromo-3-heptanoylthiophene (78). To a solution of 3-heptanoylthiophene (**60**) (0.30



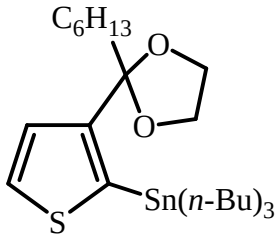
g, 1.5 mmol) in 2 mL of dry DMF was added N-bromosuccinimide (NBS) (0.32 g, 1.8 mmol). The mixture was heated for three days at 85 °C. After cooling to room temperature the mixture was passed through a filter syringe (0.2 μM), then washed with saturated $NaHCO_3$ (2 x 10 mL), saturated NaCl (2 x 10 mL) and water (2 x 10 mL) and then dried over $MgSO_4$. The solvent was removed and the product mixture was subjected to flash chromatography, hexane:EtOAc (9:1). The product was obtained 52% yield (0.22

g) as a pale yellow solid, mp 48-49 ˚C. ^{1}H NMR: ($CDCl_3$) δ 7.90 (d, *J* = 1.6, 1H), δ 7.48 (d, *J* = 1.6, 1H), δ 2.80 (t, *J* = 7.3 Hz, 2H), δ 1.70 (p, *J* = 7.3 Hz, 2H), δ 1.38-1.28 (m, 6H), δ 0.89 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR: ($CDCl_3$) (^{1}H decoupled) δ 193.8, 142.7, 132.7, 129.6, 113.6, 39.5, 31.7, 29.0, 24.3, 22.6, 14.1. IR (KBr, cm^{-1}) 3313, 3082, 2926, 2857, 1666, 1512, 1464, 1423, 1404, 1286, 1230, 1189, 1173, 997, 974, 879, 860, 850, 786, 726, 654, 627. Anal. Calcd. for $C_{11}H_{15}OSBr$: C 48.01; H 5.49. Found: C 47.72; H 5.33.

2-Hexyl-2-thiophen-3-yl-[1,3]dioxalane (79). 3-Heptanoylthiophene (**60**) (98.1 mg, 0.5 mmol), ethylene glycol (0.31 g, 5.0 mmol) and few crystals of PTSA were dissolved in benzene (10 mL) in a round-bottomed flask connected to a Dean-Stark trap. The solution was refluxed and the water-benzene azeotrope was continuously drained until it did not appear cloudy. After cooling to room temperature the benzene layer was separated from the ethylene glycol and dried over $MgSO_4$. The solvent was removed by rotary evaporation and the product was used on the next step without further purification.



2-(2-Tri-*n*-butylstannylthiophen-3-yl)-2-hexyl-1,3-dioxolane (80). To a solution of 2-hexyl-2-thiophen-3-yl-[1,3]dioxalane (**79**) (0.50 g, 2.0 mmol) in 5 mL of dry THF at -78 ^{o}C was added *n*-butyllithium (1.40 mL of 1.43 M solution in hexane, 2 mmol). After stirring for 30 min, then tri-*n*-butylstannyl chloride (0.68 g, 2 mmol) was added by syringe all at once. The solution was allowed to warm to -50 ^{o}C and kept at that temperature for 3 hours. After which 50 mL of saturated NaCl solution was added, followed by extraction with dichloromethane (3 x 20 mL). The solvent was removed by

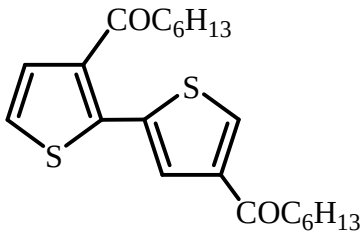


rotary evaporation and the mixture was subjected to flash chromatography, 2% triethylamine:hexane. The product **80** was collected and used in the following reaction without further purification since the ^{1}H NMR showed that tri-*n*-butylstannyl chloride impurities were not removed from the product mixture. ^{1}H NMR ($CDCl_3$) δ 7.50 (d, *J* = 4.7, 1H, Sn, I = 0), 7.21 (d, *J* = 4.7, 1H), 3.97(m, 2H), 3.80 (m, 2H), 1.84 (m), 1.5-1.21(bm), 1.10 (m), 0.94- 0.78 (bm).

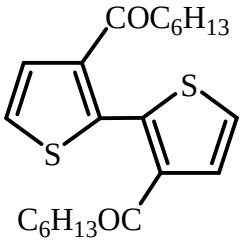
2-Iodo-3-heptanoylthiophene (81). To a solution of 2-hexyl-2-thiophen-3-yl-[1,3]dioxalane (**79**) (0.25 g, 1.04 mmol) in THF (2 mL) was added *n*-butyllithium (0.90 mL, 1.40 M, 1.26 mmol) at -78°C. Iodine (0.27 g, 1.06 mmol) in THF (3 mL) was added dropwise. When the addition was complete the mixture was allowed to warm to room temperature and was poured into cold 1M HCl (5 mL). The mixture was diluted with ether (10 mL), the organic layer was separated and the aqueous layer was extracted with ether (2 x 10 mL). The combined organic layers were washed with 1M solution of sodium thiosulfate (2 x 10 mL), water (2 x 10mL) and dried over $MgSO_4$. The solvent was removed by rotary evaporation. The product 2-iodo-3-heptanoylthiophene (**81**) was obtained in quantitative yield (0.35 g) as a yellow oil. ^{1}H NMR: ($CDCl_3$) δ 7.44 (d, *J* = 5.6, 1H), δ 7.25 (d, *J* = 5.6, 1H), δ 2.88 (t, *J* = 7.3 Hz, 2H), δ 1.69 (p, *J* = 7.3 Hz, 2H), δ 1.38-1.24 (m), δ 0.87 (m). ^{13}C NMR: ($CDCl_3$) (^{1}H decoupled) δ 195.4, 141.9, 131.9, 128.5, 79.9, 41.5, 31.7, 29.0, 24.1, 22.6, 14.1. IR (KBr, cm^{-1}) 3102, 2954, 2927, 2856, 1680, 1501, 1395, 713. HRMS (m / z): $[M + H]^+$ calcd for $C_{11}H_{16}IOS$, 322.9922; found, 322.9950.The compound

was used in the next step without further purification because the compound is unstable and releases iodine when subjected to flash chromatography.

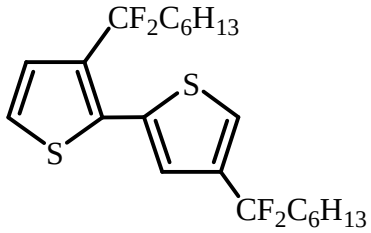
3,4'-diheptanoyl -2,2'-bithiophene (82). 5-Bromo-3-heptanoylthiophene (**77**) (0.55 g, 2.0 mmol) and 2-(2-tri-*n*-butylstannylthiophen-3-yl)-2-hexyl-1,3-dioxolane (**80**) (1.6 g, 3.0 mmol) was dissolved in 3 mL of dry DMF. Copper(I) iodide (95 mg, 0.5 mmol), triphenylphosphine (0.10 g, 0.40 mmol) and $Pd_2(dba)_3$ (91.6 mg, 0.1 mmol) was added and the mixture which was heated at 80 ˚C for 24 h. The mixture was cooled to room temperature, filtered and subjected to flash chromatography using 0-10% ethyl acetate / hexane to give 0.31 g (40% yield) of **82** as pale yellow oil. ^{1}H NMR ($CDCl_3$) δ 8.06 (d, *J* = 1.4, 1H), δ 7.75 (d, *J* = 1.4, 1H), δ 7.40 (d, *J* = 5.4, 1H), δ 7.26 (d, *J* = 5.4, 1H, overlapped with $CHCl_3$), δ 2.86 (t, *J* = 7, 2H), δ 2.77 (t, *J* = 7, 2H), δ 1.72 (p, *J* = 7.3, 2H), δ 1.64 (p, *J* = 7.3, 2H), δ 1.40-1.19 (m, 12H), δ 0.89 (t, *J* = 7.0, 3H), δ 0.86 (t, *J* = 6.9, 3H). ^{13}C NMR: ($CDCl_3$) (^{1}H decoupled) δ 197.1, 194.8, 142.0, 140.3, 137.3, 135.3, 133.5, 129.2, 128.6, 125.1, 42.2, 39.8, 31.7_5, 31.6_9, 29.1_3, 28.9_8, 24.4, 24,3, 22.6_3, 22.5_8, 14.1_5, 14.1_3. MS [EI]; 390.4 (M^+), 320.3 (McLafferty rearrangement M^+-C_5H_{10}), 305.3 (M^+- C_6H_{13}), 277.3 (M^+- COC_6H_{13}), 195.3(M^{+2}). IR (KBr, cm^{-1}) 3103, 2956, 2930, 2860, 1677, 1527, 1504, 1459, 1409, 1383, 1233, 1169, 872, 723. HRMS (m / z): $[M + H]^+$ calcd for $C_{22}H_{31}O_2S_2$, 391.1721; found, 391.1754.



3,3'-diyl)diheptanoyl -2,2'-bithiophene (83). 2-Iodo-3-heptanoylthiophene (**81**) (0.161 g, 0.50 mmol) was dissolved in 0.5 mL of dry DMF, copper powder (0.255 g, 4.0 mg-atom) was added, and the mixture was heated at 145 ^{o}C under an argon atmosphere for 24 hours. The reaction mixture was cooled, dissolved in 10 mL of $CHCl_3$, filtered through celite in a glass frit funnel, then the solvent was removed by rotary evaporation and the crude was chromatograghed over silica gel using hexane:EtOAc (10:1) to afford **83** in 66% yield (0.13 g) as a yellow oil. ^{1}H NMR ($CDCl_3$) δ 7.46 (d, *J* = 5.5, 1H), 7.35 (d, *J* = 5.5, 1H), 2.59 (t, *J* = 7.5 Hz, 2H), 1.54 (p, *J* = 7.2 Hz, 2H), 1.28-1.15 (bm, 6H), 0.83 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR: ($CDCl_3$) (^{1}H decoupled) δ 196.0, 140.2, 138.7, 128.7, 126.4, 41.4, 31.7, 28.9, 23.9, 22.6, 14.1. IR (KBr, cm^{-1}) 3106, 3088, 2954, 2930, 2858, 1680, 1540, 1502, 1461, 1402, 1378, 1273, 1237, 1213, 1063, 873, 860, 722. HRMS (m / z): $[m + H]^{+}$ calcd for $C_{22}H_{31}O_2S_2$, 391.1721; found, 391.1723.

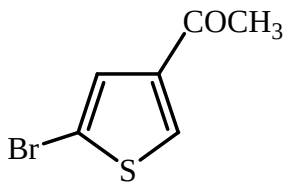


3,4'-bis(1,1-difluoroheptyl)-2,2'-bithiophene (59). Dimer **82,** (0.20 g, 0.51 mmol) was transferred to a 125 mL plastic bottle and DAST (1 mL, 7.4 mmol) was added. The mixture was stirred under argon at 40-50 °C for four days. The cooled reaction mixture was extracted with diethyl ether (4 x 15 mL) and washed carefully with saturated sodium bicarbonate until free of acid. The extract was dried over $MgSO_4$ and the solvent was removed by rotary evaporation. The crude product was passed through a short silica gel plug (5 cm). The product **59** was obtained in 20% yield (44.0 mg) as a colorless oil. ^{1}H NMR ($CDCl_3$) δ 7.48 (d, *J* = 1.0, 1H), δ 7.29 (d, *J* =

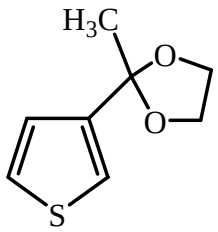


5.4, 1H), δ 7.20 (d, *J* = 1.0, 1H), δ 7.16 (d, *J* = 5.4, 1H), δ 2.13 (m, 2H), δ 1.98 (m, 2H), δ 1.44 (m, 2H), δ 1.36-1.14 (m, 14) δ 0.87 (t, *J* = 7, 3H), δ 0.83 (t, *J* = 7, 3H). ^{13}C NMR: ($CDCl_3$) (^{1}H decoupled) δ 139.3 (t, *J* = 30.0), 135.6 (t, *J* = 29.0), 134.9, 133.6, 127.5 (t, *J* = 5.8), 126.6, 125.6, 125.1 (t, *J* = 6.5), 122.0 (t, *J* = 241.4), 121.2 (t, *J* = 241.5), 38.7 (t, *J* = 26.5), 37.8 (t, *J* = 26.4), 31.7, 31.4, 29.0, 28.8, 22.6, 22.5, 14.1, 14.0, 11.2. ^{19}F NMR: (282.8 MHz), ($CDCl_3$), ($CFCl_3$), δ -91.2 (t, *J* = 16.1 Hz), -85.2 (t, *J* = 16.5 Hz). IR (KBr, cm^{-1}) 3114, 3003, 2928, 2855, 1385, 1276, 1247, 1171, 1128, 916, 866, 834.6, 739, 665.

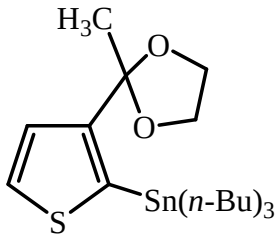
3-Acetyl-5-bromothiophene (84).[140] To 3-acetyl thiophene (**85**) (3.15 g, 25 mmol) in of glacial acetic acid (12.5 mL) was added sodium acetate (2.25 g, 27.5 mmol). The mixture was stirred vigorously and bromine (4.0g, 25 mmol) in 10 mL of glacial acetic acid was added slowly over 15 min. The reaction was stirred at room temperature overnight. The reaction mixture was diluted with ethyl acetate (50 mL) then washed with 1 M sodium thiosulphate (2 x 10 mL). The organic layer was separated, washed with sodium bicarbonate (3 x 20 mL), water (2 x 20 mL) and dried over $MgSO_4$. The solvent was removed and the crude product was subjected to flash chromatography using hexane:EtOAc (9:1). The product **83** was collected in 52% yield (2.67 g) as a white solid, mp 62-64 °C, [Lit.[140] 63-64 °C]. ^{1}H NMR ($CDCl_3$) δ 7.90 (d, *J* = 1.8, 1H), δ 7.48 (d, *J* = 1.8, 1H), 2.48 (s, 3H). ^{13}C NMR: ($CDCl_3$) (^{1}H decoupled) δ 190.9, 142.7, 133.3, 129.4, 113.6, 26.9.



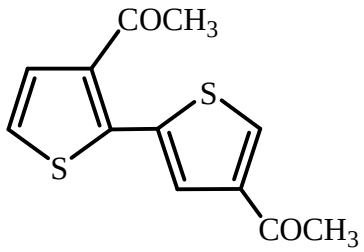
2-Methyl-2-thiophen-3-yl-[1,3]dioxalane (86). The compound **86** was prepared similar to **79** and used in the next step without purification.



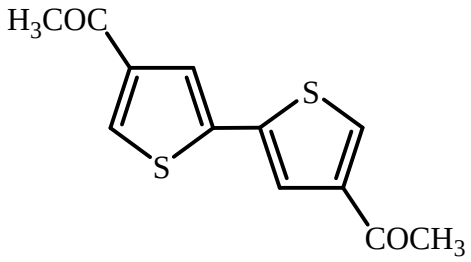
2-(2-Tri-*n*-butylstannylthiophen-3-yl)-2-methyl-1,3-dioxolane (87). Compound **86** was prepared similar to **80**, and was obtained as a colorless oil and used in the next step without purification.



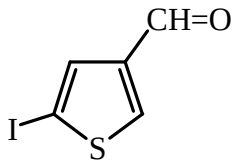
3,4'-diethanoyl -2,2'-bithiophene (88). Compound **88** was prepared in 65% yield (0.33 g) similar to **82**, and was obtained as a pale yellow solid mp 86-88 °C. ^{1}H NMR ($CDCl_3$) δ 8.08 (d, *J* = 1.4, 1H), δ 7.77 (d, *J* = 1.4, H), δ 7.43 (d, *J* = 5.5, 1H), δ 7.28 (d, *J* = 5.5, 1H), δ 2.54 (s, 3H), δ 2.47 (s, 3H). ^{13}C NMR: ($CDCl_3$) (^{1}H decoupled) δ 193.9, 192.0, 142.2, 137.5, 135.3, 134.2, 129.7, 128.8, 125.1, 29.9, 27.4. MS [EI]; 249.9 (M^+), 235.1, 217.1, 193.0. IR (KBr, cm^{-1}) 3316, 3104, 3086, 3006, 2966, 2920, 2859, 1672, 1535, 1502, 1416, 1395, 1372, 1351, 1266, 1231,1197, 1134, 1081, 1015, 977, 924, 876, 843, 800, 736, 727, 702, 657. Anal. Calcd. for $C_{12}H_{10}O_2S_2$: C 57.57; H 4.03. Found: C 57.74; H 4.38.



4,4'-diethanoyl -2,2'-bithiophene (89). Compound **89** was prepared in 65% (0.11 g) yield using the Ullmann coupling similar to **83**, and was obtained as a white solid mp 95-97 °C. ^{1}H NMR ($CDCl_3$) δ 7.94 (d, *J* = 1.4, 1H), δ 7.60 (d, *J* = 1.4, 1H), 2.54 (s, 3H). ^{13}C NMR: ($CDCl_3$) (^{1}H decoupled) δ 191.9, 143.2, 137.2, 131.7, 123.8, 27.3. MS [EI]; 250.1 (M^+), 235.1, 219.1, 207, 163.0. IR (KBr, cm^{-1}) 3309, 3110, 3083, 3051, 1667, 1558, 1511, 1408, 1211, 1173, 1073, 1015, 973, 926, 877, 822, 636, 599. Anal. Calcd. for $C_{12}H_{10}O_2S_2$: C 57.57; H 4.03. Found: C 57.19; H 4.27.

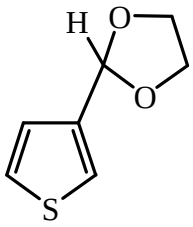


5-Iodothiophene-3-carboxaldehyde (91).[111] To a solution of thiophene-3-carboxaldehyde (**69**) (1.12, 10.0 mmol) in CCl_4 (8 mL), H_2O (6 mL) and concentrated H_2SO_4 (1 mL) in acetic acid (8 mL) was added. To the resulting solution are added HIO_3 (0.88 g, 5.0 mmol) and I_2 (1.27 g, 5.0 mmol). The solution was refluxed for 6 h, then was cooled to room temperature, and $CHCl_3$ (50 mL) was added. The layers were separated, and the aqueous layer was extracted with $CHCl_3$ (3 x 30 mL). The organic layers were combined and washed with 0.5 M $Na_2S_2O_3$ (30 mL), saturated $NaHCO_3$ (30 mL), and saturated NaCl (30 mL). The organic layer was dried over $MgSO_4$, filtered, and the solvent was removed by rotary evaporation. The crude product was purified by column chromatography (Hexane/EtOAc, 9:1). 5-iodothiophene-3-carboxaldehyde (**82**) was recrystallized from hexane and was obtained in 23% yield (0.55 g) as a pale yellow solid, mp: 68-70 °C (Lit.[112] 74 °C). ^{1}H NMR (300.5 MHz) ($CDCl_3$) δ 9.79 (s, 1H), 8.10 (d, *J* = 1.4, 1H), 7.70

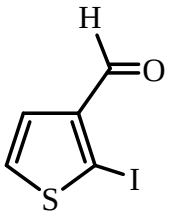


(d, J = 1.4, 1H). [Lit.[111] ^{1}H NMR ($CDCl_3$) δ 9.78 (s, 1H), 8.10 (s, 1H), 7.69 (s, 1H)]. ^{13}C NMR: ($CDCl_3$) (^{1}H decoupled) δ 183.1, 144.4, 141.9, 134.9, 76.4.

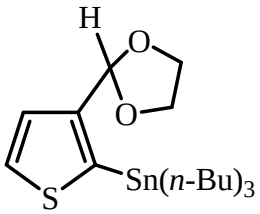
2-Thiophen-3-yl-[1,3]dioxalane (92). Compound **92** was prepared in similar manner to **79** and was obtained in quantitative yield which was used in the next step.



2-Iodothiophene-3-carboxaldehyde (93).[113] To a solution of 2-thiophen-3-yl-[1,3]dioxalane (**92**) (1.0 g, 6.40 mmol) in 10 mL of THF was added *n*-butyllithium (4.7 mL, 1.5 M, 7.0 mmol) at room temperature then the mixture was cooled to -78 °C. Iodine (1.79 g, 7.0 mmol) in 30 mL of THF was added dropwise, which caused immediate decolorization of the iodine color. When the addition was complete the mixture was poured into 25 mL of cold 1M HCl. The organic layer was separated and the aqueous layer was extracted with ether (2 x 50 mL). The combined organic layers were washed with 1M solution of sodium thiosulfate (2 x 50 mL), water (2 x 50mL) and dried over $MgSO_4$. The solvent was removed by rotary evaporation. The product 2-iodothiophene-3-carboxaldehyde (**93**) was recrystalized from hexane and 1.0 g (65%) was obtained as a colorless solid which change to black tar upon storage in a glass vial. ^{1}H NMR ($CDCl_3$) δ 9.73 (s, 1H), 7.50 (d, J = 5.5), 7.32 (d, J = 5.5, 1H). Lit.[112] ^{1}H NMR ($CDCl_3$) δ 9.78 (s, 1H) 8.10 (s, 1H), 7.69 (s, 1H). ^{13}C NMR: ($CDCl_3$) (^{1}H decoupled) δ 186.9, 141.7, 132.0, 126.9, 88.8.

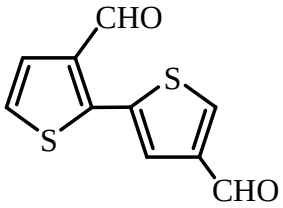


2-(2-Tri-*n*-butylstannyl thiophen-3-yl)-1,3-dioxolane (94). Compound **94** was prepared



in quantitative yield (0.9, g) similar to **80** and was obtained as a colorless oil. ^{1}H NMR ($CDCl_3$) δ 7.54 (d, *J* = 4.6, 1H), 7.27 (d, *J* = 5.0, 1H), 5.71 (s, 1H) 4.06 (m, 2H), 3.96 (m, 2H), 1.50 (m, 6H), 1.29(m, 6H), 1.08 (m, 6H), 0.85 (t, *J* = 7.3, 9H). Lit.[141] ^{1}H NMR ($CDCl_3$) δ 7.31 (d, 1H, H_4, *J* = 5.17 Hz), 5.80 (s, 1H, CH), 4.05 (m, 4H, CH_2CH_2), 1.52-1.87 (m, 27, (*n*-Bu)$_3$). ^{13}C NMR: ($CDCl_3$) (^{1}H decoupled) δ 146.2, 136.2, 131.2, 127.2, 102.0, 65.0, 29.0, 27.2, 13.6, 11.5.

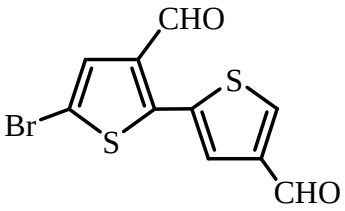
2,2'-Bithiophene-3,4'-dicarbaldehyde (95). 5-Iodothiophene-3-carboxaldehyde (**91**)



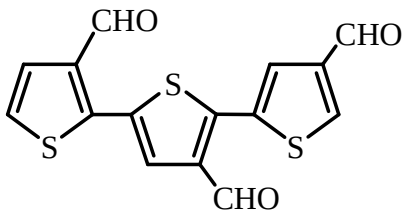
(0.42 g, 2.0 mmol) and 2-(2-tri-*n*-butylstannyl thiophen-3-yl)-1,3-dioxolane (**94**) (1.34 g, 3.0 mmol) was dissolved in 3 mL of dry DMF. Copper(I) iodide (95 mg, 0.5 mmol), triphenylphosphine (0.10 g, 0.40 mmol) and $Pd_2(dba)_3$ (91.6 mg, 0.1 mmol) was added and the mixture which was heated at 80 ˚C for 24 h. The mixture was cooled to room temperature, filtered and subjected to flash chromatography 0-10% ethyl acetate / hexane to give of **95** in 57% yield (0.25 g) which was obtained as a white solid, mp 100-102 °C. ^{1}H NMR ($CDCl_3$) δ 10.10 (s, 1H), 9.93 (s, 1H) 8.23 (d, *J* = 1.0, 1H), 7.71 (d, *J* = 1.0, 1H), 7.57 (d, *J* = 5.5, 1H), 7.33 (d, *J* = 5.5, 1H). ^{13}C NMR: ($CDCl_3$) (^{1}H decoupled) δ 184.5_4, 184.4_8, 145.0_6, 143.5, 138.1_8, 138.0_9, 134.7, 127.8, 126.8, 126.3. MS [EI]; 222.0 (M^+), 193.1 (M^+-CHO), 165.0 (M^+-C_2O_2H), 165.0, 149.0, 138.0, 121.1. IR (KBr, cm^{-1}) 3317, 3113, 3086, 2895, 2837, 2808, 2735, 1671, 1539, 1500, 1429, 1386, 1359, 1230, 1082,

1069, 943, 903, 827, 738, 687, 613. Anal. Calcd. for $C_{10}H_6O_2S_2$: C 54.03; H 2.72. Found: C 54.01; H 2.69

5-Bromo-2,2'-bithiophene-3,4'-dicarbaldehyde (96). To a solution of 2,2'-Bithiophene-3,4'-dicarbaldehyde (**95**) (0.2 g, 0.66 mmol) in 1 mL of dry DMF was added N-bromosuccinimide (NBS) (0.14 g, 0.8 mmol). The mixture was heated for three days at 85 °C. After cooling to room temperature the mixture was passed through a filter syringe (0.2 μM), then washed with saturated $NaHCO_3$ (2 x 10 mL), saturated NaCl (2 x 10 mL) and water (2 x 10 mL) and then dried over $MgSO_4$. The solvent was removed by rotary evaporation and the product mixture was subjected to flash chromatography using hexane:EtOAc (9:1). The product **96** was obtained in 53% yield (0.11 g) as a white solid, mp 133-134 °C. ^{1}H NMR ($CDCl_3$) δ 9.96 (s, 1H), 9.91 (s, 1H) 8.22 (d, *J* = 1.3, 1H), 7.67 (d, *J* = 1.3, 1H), 7.51 (s, 1H). ^{13}C NMR: ($CDCl_3$) (^{1}H decoupled) δ 184.3, 183.1, 146.0, 143.5, 138.5, 138.4, 133.3, 130.0, 127.2, 114.1. MS [EI]; 300.0 (M^+), 301.9 (M^++2), 272.9 (M^++2-CHO), 222 (M^+-Br), 193, 165, 141, 121. IR (KBr, cm^{-1}) 3326, 3109, 3082, 3046, 2877, 2851, 2828, 2790, 1674, 1544, 1511, 1466, 1434, 1405, 1359, 1205, 1182, 1173, 1139, 1000, 979, 923, 872, 845, 777, 731, 685, 673.3. HRMS (m / z): $[M]^+$ calcd for $C_{10}H_5BrO_2S_2$, 299.8914; found, 299.9085.

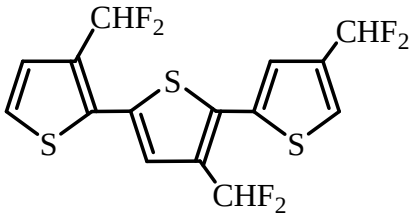


3,4',4''-Tri-formyl-2,2':5',2''-terthiophene (97). 5-Bromo-2,2'-bithiophene-3,4'-dicarbaldehyde (**96**) (0.10 g, 0.33 mmol) and 2-(2-tri-*n*-butylstannyl thiophen-3-yl)-1,3-dioxolane (**94**) (0.22 g, 0.5 mmol) was dissolved in 1 mL of dry



DMF. Copper(I) iodide (6 mg, 0.03 mmol), triphenylphosphine (0.01 g, 0.04 mmol) and $Pd_2(dba)_3$ (27.3 mg, 0.1 mmol) was added and the mixture which was heated at 80 ˚C for 24 h. The mixture was cooled to room temperature, filtered and subjected to flash chromatography using 0-20% ethyl acetate / hexane. The trimer **97** was obtained in 54% yield (59.0 mg) as a yellow solid, mp 170-171 °C. ^{1}H NMR ($CDCl_3$) δ 10.14 (s, 1H), 10.11 (s,1 H), 9.94 (s, 1H), 8.27 (d, *J* = 1.3, 1H), 7.78 (d, *J* = 1.3, 1H), 7.73 (s, 1H), 7.57 (d, *J* = 5.4, 1H), 7.34 (d, *J* = 5.4, 1H). ^{13}C NMR: ($CDCl_3$) (^{1}H decoupled) δ 184.3_2, 184.2_9, 184.1, 146.5, 144.0, 143.6, 138.6, 138.3, 138.1, 133.6, 133.2, 128.8, 128.3, 127.4, 126.5. IR (KBr, cm^{-1}) 3321, 3117, 3095, 3053, 2885, 2860, 1674, 1552, 1528, 1508, 1388, 1369, 1356, 1231, 1192, 1181, 1128, 1080, 998, 959, 940, 886, 836, 790, 738, 715. HRMS (m / z): $[M + H]^+$ calcd for $C_{15}H_9O_3S_3$, 332.9714; found, 332.9760.

3,4',4''-Tris(difluoromethyl)-2,2':5',2''-terthiophene (90). Trimer **97** (70 mg, 0.21 mmol) was treated with DAST (0.25 mL, 1.85 mmol) in plastic bottle. The mixture was stirred at room temperature for 24 hours,then reaction mixture was diluted with ether (5 mL). The ether layer was passed through a short silica gel plug (5 cm). The product was collected in quantitative yield (83 mg) as a white solid, mp 95-96 °C. ^{1}H NMR ($CDCl_3$) δ 7.65 (d, *J* = 1.4, 1H), 7.38 (d, *J* = 5.4, 1H) 7.35 (s, 1H), 7.33 (d, *J* = 5.5, 1H), 7.30 (s, 1H), 6.75 (t, d, *J* = 55.0, 1H, CHF_2) 6.69 (two overlaped triplets, d, *J* = 56.3, *J* = 54.8, 2H, CHF_2). ^{19}F NMR: ($CDCl_3$), ($CFCl_3$) δ -106.79 (d, *J* = 54.7 Hz), δ -107.35 (d, *J* = 54.7 Hz), δ -109.85 (dd, *J* = 56.1 Hz, *J* = 2.2 Hz). IR (KBr, cm^{-1}) 3127, 3115, 3082, 3009, 2987, 2967, 2919, 1570, 1532,



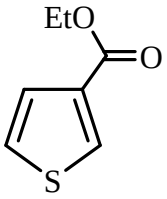
1477, 1417, 1399, 1362, 1351, 1319, 1251, 1194, 1162, 1108, 1086, 1042, 1006, 985, 931, 869, 849. 837, 772, 724, 657. HRMS (m / z): $[M + H]^+$ calcd for $C_{15}H_9F_6S_3$, 398.9726; found, 398.9794.

2-Bromothiophene-4-carboxylic acid (100).[109] A solution of bromine (2.10 mL, 40.0 mmol) in glacial acetic acid (50 mL) was added dropwise over two hours to a stirred solution of thiophene-3-carboxylic acid (**99**) (5.12 g, 40.0 mol) in glacial acetic acid (50 mL). The reaction was stirred for 30 min at room temperature. The mixture was poured into 200 mL of ice-water and solid Na_2SO_3 was added to decolorize. The white precipitate was filtered and recrystalized from 250 mL of hot water. The product **100** was obtained in 42% yield (3.5 g) as white solid, mp 139-141 °C (lit.[109] 140-141 °C). ^{1}H NMR ($CDCl_3$) δ 11.70 (bs, 1H), δ 8.11 (d, *J* = 1.5 Hz, 1H), δ 7.51 (d, *J* = 1.5 Hz, 1H). [lit.[109] ^{1}H NMR ($CDCl_3$) δ 10.27 (s), 8.12 (d, *J* = 1.0 Hz), δ 7.51 (d, *J* = 1.0 Hz).]. ^{13}C NMR ($CDCl_3$) (^{1}H decoupled) δ 166.7, 135.8, 133.1, 130.4, 113.3. [lit.[109] ^{13}C NMR ($CDCl_3$) δ 166.8, 135.8, 133.1, 130.4, 113.4].

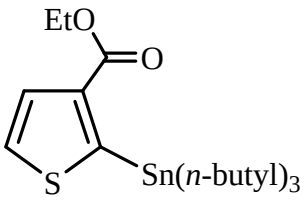
Ethyl 2-bromothiophene-4-carboxylate (101). 2-Bromothiophene-4-carboxylic acid (**100**) (1.5 g, 11.7 mmol) with toluene (30 mL), ethanol (50 mL) and concentrated sulfuric acid (1 mL) was refluxed in a one-necked round-bottomed flask attached to a Dean-Stark trap. For the first five hours 20 mL were withdrawn from the Dean-Stark trap every hour and an equal volume of ethanol-toluene was added to the reaction mixture. The reaction mixture was cooled to room temperature and the solvent was removed under reduced pressure. The

product was extracted with hexane (3 x 50 mL) and dried over $MgSO_4$. The solvent was removed and the product was collected as a yellow oil in quantitative yield (2.75 g). ^{1}H NMR ($CDCl_3$) δ 7.97 (d, *J* = 1.5 Hz, 1H), δ 7.46 (d, *J* = 1.5 Hz, 1H), δ 4.30 (q, *J* = 7.2 Hz, 2H), δ 1.35 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$) (^{1}H decoupled) δ 162.8, 133.9, 132.4, 127.9, 125.8, 60.6, 14.3. IR (KBr, cm^{-1}) 3107, 2978, 1717, 1528, 1422, 1230, 1095, 1020, 980, 735.

Ethyl thiophene-3-carboxylate (102). The esterfication took place similar to the previous reaction. The product which was distilled under vacuum (b.p. 47-49 °C, 0.1 mm Hg) and collected as colorless oil in quantitative yield. ^{1}H NMR ($CDCl_3$) δ 8.08 (dd, *J* = 3.0, 1.3 Hz, 1H), δ 7.51 (dd, *J* = 5.0, 1.3 Hz, 1H), δ 7.28 (dd, *J* = 5.0, 3.0 Hz, 1H), δ 4.30 (q, *J* = 7.1 Hz, 2H), δ 1.35 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$) (^{1}H decoupled) δ 162.6, 133.8, 132.3, 127.7, 125.7, 60.4, 14.2. IR (KBr, cm^{-1}) 3110, 2982, 2933, 2904, 2873, 1715, 1521, 1409, 1260, 1190, 1101, 1018, 934, 877, 823, 750, 697.



Ethyl 2-(tri-*n*-butylstannyl)thiophene-3-carboxylate (103). To a solution of diisopropylamine (0.78 g, 7.7 mmol) in 10 mL of dry THF at -78˚C was added *n*-butyllithium (4.8 mL, 1.6 M, 7.7 mmol) under an argon atmosphere. After stirring for 25 min, a solution of ethyl thiophene-3-carboxylate (**102**) (1.0 g, 6.4 mmol) in 10 mL of THF was added slowly over 10 min. The mixture was allowed to stand at -78˚C for an additional 30 min, and then tri-*n*-butylstannyl chloride (2.5 g, 7.7 mmol) was added by syringe all at once. The cooling bath was removed, and the solution was allowed to warm to room

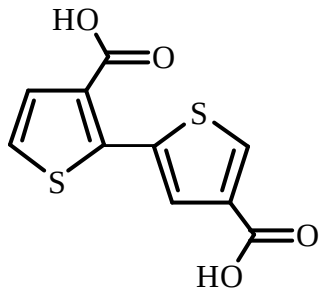


temperature over 3 h, after which 100 mL of saturated NaCl solution was added followed by extraction with dichloromethane (3 x 10 mL). The organic layer was dried over $MgSO_4$ and concentrated then subjected to flash chromatography 2% triethyl amine / hexane give the product as red oil which was used in the next step without further purification since ^{1}H NMR showed that tin impurities was not completely removed. ^{1}H NMR ($CDCl_3$) δ 7.67 (d, *J* = 5.0, 1H), 7.54 (d, *J* = 5.0, 1H), 4.32 (q, *J* = 7.0, 2H) 4.10 (m, 2H), 1.5 (m), 1.40-1.26 (m), 1.19-1.07 (m), 0.87 (m).

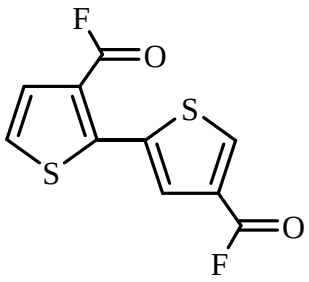
Diethyl 2,2'-bithiophene-3,4-dicarboxylate (104). Ethyl 2-bromothiophene-4-carboxylate (**101**) (1.17 g, 5.0 mmol) and ethyl 2-(tri-*n*-butylstannyl)thiophene-3-carboxylate (**103**) (3.34 g, 7.5 mmol) was dissolved in 3 mL of dry DMF. Copper(I) iodide (95 mg, 0.5 mmol), triphenylphosphine (0.10 g, 0.40 mmol) and $Pd_2(dba)_3$ (91.6 mg, 0.1 mmol) was added and the mixture was heated at 80 ˚C for 24 h. The mixture was cooled to room temprature, filtered and subjected to flash chromatography ethyl hexane:EtOAc (0-10%) to give **104** in 60% yield (0.94 g) as a pale yellow powder, mp 54-55 ˚C. ^{1}H NMR ($CDCl_3$) δ 8.14 (d, *J* = 1.3, 1H), δ 7.75 (d, *J* = 1.3, 1H), δ 7.49 (d, *J* = 5.4, 1H), δ 7.22 (d, *J* = 5.4, 1H), δ 4.34 (t, *J* = 7, 2H), δ 4.28 (t, *J* = 7, 2H), δ 1.36 (t, *J* = 7, 3H), δ1.29 (t, *J* = 7, 3H). ^{13}C NMR ($CDCl_3$) (^{1}H decoupled) δ 162.9, 162.5, 134.6, 134.1, 133.4, 130.4, 129.4, 128.8, 124.5, 60.9, 60.8, 14.3, 14.1. MS [EI]; 310.1 (M^+), 295.1, 282.1, 265.0, 254.0, 237.0, 219.1, 192.1. IR (KBr, cm^{-1}) 3379, 3115, 3095, 2986, 2941, 2907, 2872, 1702, 1532, 1381, 1353, 1265,

1231, 1201, 1159, 114, 1100, 1087, 1029, 968, 936, 872, 838, 786, 772, 743, 723. Anal. Calcd. for $C_{14}H_{14}O_4S_2$: C 54.17; H 4.55. Found: C 54.32; H 4.42.

2,2'-Bithiophene-3,4-dicarboxylic acid (105). Diethyl 2,2'-bithiophene-3,4-dicarboxylate (**103**) (0.31 g, 1.0 mmol) was suspended in water (5 mL) and potassium hydroxide (0.3 g, 5.3 mmol). The mixture was refluxed for eight hours, cooled to room temperature and acidified with 6 M hydrochloric acid (5 mL). The product was filtered and dried to give **105** in 94% yield (0.24 g) as white solid, mp 282-284 °C. ^{1}H NMR (DMSO-d_6) δ 12.93 (bs, 2H), δ 7.07 (s, 1H), δ 3.62 (t, *J* = 8.0 Hz, 4H), δ 2.95 (d, *J* = 8.0 Hz, 4H). ^{13}C NMR (DMSO-d_6) (^{1}H decoupled) δ 163.9, 163.2, 140.3, 135.0, 134.5, 133.9, 130.6, 129.3, 128.8, 125.9. MS [EI]; 254.1 (M^+), 237.0, 219.1, 210.0, 192.1, 165.1, 149.1. IR (KBr, cm^{-1}) 2100-3700 (broad –OH), 1682, 1574, 1516, 1470, 1434, 1359, 1281, 1191, 1178, 1102, 1087, 963, 924, 886, 856, 832, 792, 746, 738, 692. Anal. Calcd. for $C_{10}H_6O_4S_2$: C 47.23; H 2.38. Found: C 47.62; H 2.52.

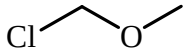


2,2'-Bithiophene-3,4'-dicarbonyl difluoride (98). 2,2'-Bithiophene-3,4-dicarboxylic acid (**105**) (0.20 g 0.79 mmol) in dichloromethane (2 mL) was transferred to a 25 mL plastic bottle and DAST (0.5 mL, 3.7 mmol) was added. The mixture was stirred at room temperature for 24 h. The reaction mixture was diluted with ether (5 mL). The ether layer was passed through a short silica gel plug (5 cm). The product was collected in 12% yield (10 mg) as a white solid, mp (to be measured). ^{1}H NMR ($CDCl_3$) δ



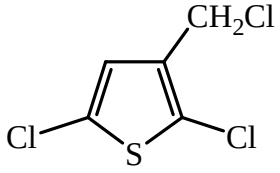
8.39 (d, *J* = 1.3 Hz 1H), δ 7.85 (d, *J* = 1.2 Hz 1H), δ 7.55 (d, *J* = 5.4 Hz 1H), δ 7.40 (d, *J* = 5.5 Hz 1H). ^{13}C NMR ($CDCl_3$) (^{1}H decoupled) δ 153.6 (d, *J* = 26.0 Hz), 150.9 (d, *J* = 25.0 Hz), 146.1 (d, *J* = 9.0 Hz), 139.4, 134.6 (d, *J* = 2.0 Hz), 130.9, 130.4 (d, *J* = 4.0 Hz), 127.8 (d, *J* = 82.0 Hz), 126.2, 122.9 (d, *J* = 77.0 Hz). ^{19}F NMR: ($CDCl_3$), ($CFCl_3$), δ -23.6 (s), -32.4 (s). IR (KBr, cm^{-1}) 3586, 3135, 3126, 3500-2300 (broad), 1801, 1543, 1509, 1458, 1421, 1385, 1372, 1250, 1197, 1110, 1050, 933, 894, 847, 730, 716, 682, 631. MS (EI) 258.0 (M^+), 238.9, 230.0, 219.0, 210.0. HRMS (m / z): $[M + H]^+$ calcd for $C_{10}H_5O_2F_2S_2$, 258.9654; found, 258.9661.

Chloromethyl methyl ether (135).[135] A 500 mL three-necked, round-bottomed flask was



equipped with a magnetic stirring bar and a reflux condenser. The flask was charged with benzoyl chloride (**136**) (281.2 g, 2.0 mol), dimethoxymethane (**137**) (152.2 g, 2.0 mol) and concentrated sulfuric acid (10.0 g, 102.0 mmol). The mixture was stirred and heated in an oil bath at 50-65°C under an argon atmosphere. After 64 hours the reaction was allowed to cool to room temperature and the product was distilled. The solution was heated slowly to about 130 ^{o}C. 112 g (70% yield) was collected as a colorless liquid (bp 54-58 °C, lit.[135] bp 55-57 °C). ^{1}H NMR ($CDCl_3$) δ 3.50 (s, 2H), 5.45 (s, 3H). [Lit.[135] ^{1}H NMR ($CDCl_3$) δ 3.52 (s), 5.46 (s)].

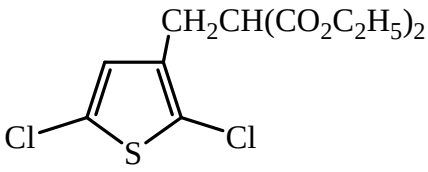
3-Chloromethyl-2,5-dichlorothiophene (138).[136] In an ice-bath cooled three-necked



round-bottomed flask fitted with an addition funnel was placed 2,5-dichlorothiophene (**139**) (26.0 g, 0.17 mol) and chloromethyl methyl ether (16 g, 0.19 mol) in 50 mL of carbon disulfide (or dry dichloromethane). Tin(IV) chloride (15.0 g, 0.057 mol) was added dropwise to the

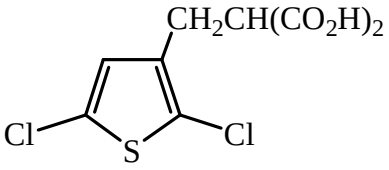
solution over half hour period. The ice-bath was removed after one hour and the reaction mixture was kept at room temperature for another two hours. The reaction mixture was diluted with 200 mL of ice-water, washed with water (4 x 100 mL) and dried over $MgSO_4$. The solvent was removed by rotary evaporation. Distillation of the product mixture under reduced pressure (bp 69-74 ºC, 1.0 mm Hg), (lit.[134] 73-74 °C, 1.0 mm Hg) afforded the product **138** as a colorless liquid in 56% yield (19.0 g). ^{1}H NMR ($CDCl_3$) δ 6.86 (s, 1H), 4.47 (s, 2H). ^{13}C NMR ($CDCl_3$) (^{1}H decoupled) δ 134.2, 127.1, 126.5, 125.4, 37.3.

Diethyl 2-((2,5-dichlorothiophen-3-yl)methyl)malonate (140).[134] Sodium hydride (60% suspension in mineral oil) (4.0 g, 0.10 mol) was placed in a three-necked round-bottomed flask fitted with a refluxing condenser and an addition funnel and then was covered with 20 mL of THF. Diethyl malonate (16.0 g, 0.10 mol) in 10 mL of THF was added to the suspension dropwise over a period of 15 min. Evolution of hydrogen was observed and the mixture was further stirred for 10 min. Then 3-chloromethyl-2,5-dichlorothiophene (**138**) (18.3 g, 0.090 mol) in 50 mL of THF was added slowly in about one hour. The mixture was further stirred for 16 hours at room temperature. Two third of the THF was removed by distillation from the mixture which was diluted with 200 mL of ice-water and extracted with ether (5 x 100 mL). The combined organic layers were dried over $MgSO_4$ and the solvent was removed by rotary evaporation. The crude product was distilled under reduced pressure (134-140 ºC, 1.0 mm Hg), (lit.[134] 135-140 °C, 0.05 mm Hg) to give 22.0 g (75 % yield) of the product **140**

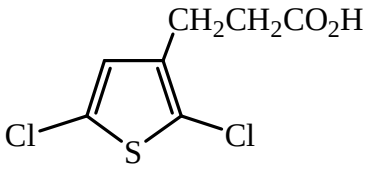


as a colorless liquid. ^{1}H NMR ($CDCl_3$) δ 6.65 (s, 1H), 4.18 (q, *J* = 7.0 Hz, 4H), 3.58 (t, *J* = 7.8 Hz, 1H), 3.10 (d, *J* = 7.8 Hz, 2H), 1.23 (t, *J* = 7.0 Hz, 6 H). [Lit.[134] ^{1}H NMR ($CDCl_3$) δ 6.67 (s, 1H), 4.19 (q, *J* = 7.0 Hz, 4H), 3.60 (t, *J* = 8.0 Hz, 1H), 3.09 (d, *J* = 8.0 Hz, 2H), 1.21 (t, *J* = 7.0 Hz, 6 H). ^{13}C NMR ($CDCl_3$) (^{1}H decoupled) δ 168.4, 134.5, 127.2, 126.2, 123.7, 61.7, 51.5, 27.0, 14.0

2-((2,5-dichlorothiophen-3-yl)methyl)malonic acid (141). Diethyl 2-((2,5-dichlorothiophen-3-yl)methyl)malonate (**140**) (7.0 g, 0.020 mol) was suspended in 50 mL of water containing potassium hydroxide (7.0 g, 0.13 mol). The mixture was refluxed for four hours, cooled and extracted with 25 mL of ether. The aqueous layer was acidified with concentrated hydrochloric acid mixed with ice and extracted with ether (4 x 50 mL), the organic layers were combined and dried over $MgSO_4$. The solvent was removed by rotary evaporation and the product **141** was obtained in 90% yield (5.2 g) as white solid, mp 136-138 °C, (lit.[134] 138-139 °C). ^{1}H NMR (DMSO-d_6) δ 12.93 (bs, 2H), 7.07 (s, 1H), 3.62 (t, *J* = 8.0 Hz, 4H), 2.95 (d, *J* = 8.0 Hz, 4H).

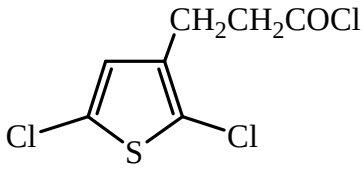


3-(2,5-Dichlorothiophen-3-yl)propanoic acid (142). 2-((2,5-Dichlorothiophen-3-yl)methyl)malonic acid (**141**) (5.2g, 0.019 mol) was distilled under reduced pressure (1.0 mm Hg). The distillate was collected over the range of 135-140 ºC, (1.0 mm Hg), (lit.[134] 150-160 °C, 1.0 mm Hg). The product **142** was obtained as white soild in 86% yield (3.75 g), mp 65-67 °C (lit.[134] 65-67 °C). ^{1}H NMR ($CDCl_3$) δ 10.7 (bs, 1H), 6.68 (s,

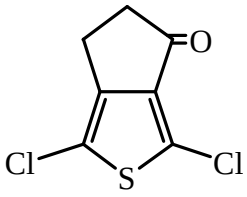


1H), 2.85 (t, *J* = 7.5 Hz, 2H), 2.62 (t, *J* = 7.5 Hz, 2H). [Lit.[134] ^{1}H NMR ($CDCl_3$) δ 11.22 (s, 1H), 6.67 (s, 1H), 3.05-2.43 (complex multiplet, 4H)].

3-(2,5-Dichlorothiophen-3-yl)propanoyl chloride (133). 3-(2,5-Dichlorothiophen-3-yl)propanoic acid (**142**) (3.75g, 0.017 mol) was dissolved in thionyl chloride (20 mL) then 2 drops of DMF was added. The mixture was refluxed for six hours and the excess thionyl chloride was distilled. The acid chloride was further purified by distillation under reduced pressure at 115-120 ºC (1.0 mm Hg), (lit.[134] 102-103 °C, 0.2 mm Hg). The acid chloride **133** was obtained as a yellow oil in 86% yield (3.5 g). ^{1}H NMR ($CDCl_3$) δ 6.64 (s, 1H), 3.14 (t, *J* = 7.5 Hz, 2H), 2.90 (t, *J* = 7.5 Hz, 2H).

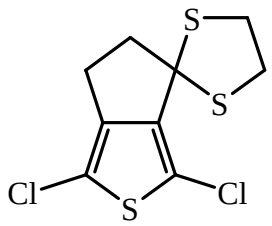


1,3-Dichloro-5,6-dihydrocyclopenta[*c*]thiophen-4-one (132). Aluminum chloride (2.6 g, 0.020 mol) was suspended in carbon disulfide (or dry dichloromethane) (30 mL) and the mixture was cooled to 0 °C using an ice-bath. To the suspension 3.4 g (0.014 mol) of the 3-(2,5-dichlorothiophen-3-yl)propanoyl chloride (**133**) dissolved in carbon disulfide (or dichloromethane) (20 mL) was added dropwise over 0.5 hour under an argon atmosphere. The ice bath was removed and the mixture was stirred at room temperature overnight. The mixture was poured into ice and concentrated hydrochloric acid (100 mL). The organic layer was separated and the aqueous layer was extracted with ether (5 x 50 mL). The combined organic layer was washed with sodium bicarbonate solution and water and dried over $MgSO_4$. The solvent was removed by rotary evaporation and a golden yellow residue was left which was distilled under reduced pressure 110-115 ºC (1.0 mm Hg),



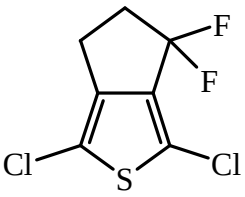
(lit.[134] 105-110 °C, 0.5 mm Hg). The distillate was recrystallized from hexane and the product **132** was obtained in 62% yield (1.8 g) as a white solid, mp 64-66 °C (lit.[134] 65-66 °C). ^{1}H NMR ($CDCl_3$) δ 3.00 (bm, 2H), 2.85 (bm, 2H). [Lit.[134] ^{1}H NMR ($CDCl_3$) δ 3.00-2.67 (complex multiplet) ^{13}C NMR ($CDCl_3$) (^{1}H decoupled) δ 195.2, 149.1, 138.8, 126.4, 118.5, 43.0, 20.5.

Spiro[1,3-dithiolane]-2,4'-1',3'-dichloro-5',6'-dihydro-cyclopenta[*c*]thiophene (143).



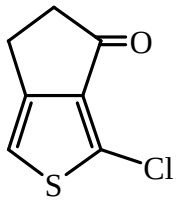
1,3-Dichloro-5,6-dihydrocyclopenta[*c*]thiophen-4-one (**132**) (0.21 g, 1.0 mmol) and 1,2-ethandithiol (0.17 mL, 2 mmol) were combined under argon and stirred, followed by the addition of borontrifluoride-acetic acid complex (1.2 g, 0.28 mL, 2 mmol). The biphasic solution was allowed to stir vigorously for 30 min. The mixture was diluted with hexane (2 mL), then the organic layer was separated and washed with saturated $NaHCO_3$ (3 x 2 mL), 1M NaOH (2 x 2 mL), saturated NaCl (2 x 2 mL) and water (2 x 2 mL). The organic extract was dried over $MgSO_4$ and the solvent removed by rotary evaporation. The mixture was subjected to flash chromatography using hexane:ethylacetate (5:1) and the product **143** was collected as a colorless oil in 95% yield (0.27 g). ^{1}H NMR ($CDCl_3$) δ 3.55 (m, 2H) δ 3.40 (m, 2H), δ 2.89 (t, J = 7.0 Hz, 2H), δ 2.67 (t, J = 7.0 Hz, 2H). ^{13}C NMR ($CDCl_3$) (^{1}H decoupled) δ 145.2, 143.1, 118.7, 116.3, 67.2, 52.4, 41.2, 25.8. IR (KBr, cm^{-1}) 2962, 2919, 2843, 1582, 1493, 1427, 1347, 1293, 1276, 1212, 1152, 1103, 1033, 941, 910, 846, 810, 732. HRMS (m / z): $[M + H]^+$ calcd for $C_9H_8Cl_2S_3$, 282.9243; found, 282.9224.

1,3-Dichloro-4,4-difluoro-5,6-dihydrocyclopenta[*c*]thiophene (125). Compound **132**



(2.07 g, 0.010 mol) was transferred to a 125 mL plastic bottle and DAST (5 mL, 0.037 mol) was added. The mixture was stirred under argon at 40-50°C for four days. The cooled reaction mixture was extracted with diethyl ether (4 x 50 mL) and washed carefully with saturated sodium bicarbonate until free of acid. The extract was dried over $MgSO_4$ and the solvent was removed by rotary evaporation. The crude product was passed through a short silica gel plug (10 cm). The product was further purified by vacuum distillation (1.2 mm Hg, 70-90°C oil-bath). The product **125** was collected as a colorless liquid in 44% yield (1.0 g). ^{1}H NMR ($CDCl_3$) δ 2.82 (m, 2H), δ 2.74 (m, 2H). ^{13}C NMR: ($CDCl_3$) (^{1}H decoupled) δ 142.8 (t, *J* = 5.0 Hz), 137.5 (t, *J* = 27.0 Hz), 123.5 (t, *J* = 246.0 Hz), 122.0, 118.3, 41.3 (bt, *J* = 25.5 Hz), 22.2. ^{19}F NMR: ($CDCl_3$), ($CFCl_3$), δ -90.4 (t, *J* = 13.0 Hz). IR (KBr, cm^{-1}) 2959, 1591, 1501, 1320, 1274, 1250, 1182, 1154, 1062, 950, 925, 610. HRMS (m / z): $[M + H]^+$ calcd for $C_7H_5F_2Cl_2S$, 228.9457; found, 228.9472.

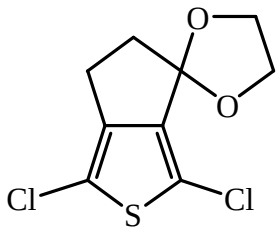
3-Chloro-5,6-dihidrorocyclopenta[*c*]thiophen-4-one (144). A solution of the dichloride



132 (0.414 g, 0.0020 mol) in 5 mL of THF, was cooled to -78 °C (Dry-ice-acetone) and treated with *n*-butyllithium (2 mL, 0.005 mol, 2.5 M in hexane). The reaction mixture was warmed to -30 °C over 4 hours. The mixture was poured into ice-water (50 mL) and the product was extracted with diethyl ether (4 x 50 mL), then the solvent was dried over $MgSO_4$, and removed by rotary evaporation. The crude product was subjected to flash chromatography using hexanes:ethyl acetate (7:3). 3-Chloro-5,6-dihidrorocyclopenta[*c*]thiophen-4-one (**144**)

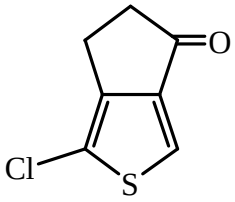
was recrystallized from hexane and was obtained in 41% yield (0.15 g) as white solid, mp dec. 97-100 °C. ^{1}H NMR ($CDCl_3$) δ 6.70 (t, *J* = 1.5 Hz, 1H), δ 2.98 (m, 2H), δ 2.91 (m, 2H). ^{13}C NMR: ($CDCl_3$) (^{1}H decoupled) δ 196.2, 153.1, 138.8, 129.5, 115.0, 43.3, 21.7. IR (KBr, cm^{-1}) 3383, 3121, 2927, 2865, 1697, 1636, 1543, 1508, 1464, 1401, 1380, 1282, 1237, 1155, 1064, 977, 964, 819, 756, 679, 622. Anal. Calcd. for C_7H_5OSCl: C 48.70; H 2.92. Found: C 48.61; H 2.89.

Spiro[1,3-dioxalane]-2,4'-1',3'-dichloro-5',6'-dihydro-cyclopenta[*c*]thiophene (146).



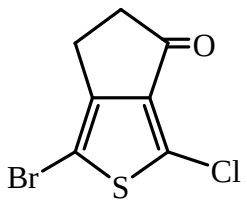
Compound **146** was prepared in similar maner to **79**. The product was used on the next step without further purification.

1-Chloro-5,6-dihydrorocyclopenta[*c*]thiophen-4-one (145). A solution of the dichloro ketal **146** (0.621 g, 0.0030 mol) in 15 mL of THF, was cooled to -78 °C (Dry-ice-acetone) and treated with *n*-butyllithium (2.25 mL, 36.0 mmol, 1.6 M in hexane). The reaction mixture was warmed to -30 °C over 4 hours. The mixture was poured into ice-water (50 mL) and the product was extracted with diethyl ether (4 x 50 mL), then the solvent was dried over $MgSO_4$, and removed by rotary evaporation. The mixture was subjected to flash chromatography using hexanes:ethyl acetate (6:4). The product was obtained in 64% yield (0.34 g) and was collected as a pale yellow solid, mp 104-107°C (lit.[138] 108 °C). ^{1}H NMR ($CDCl_3$) δ 7.60 (s, 1H), δ 3.01 (m, 2H), δ 2.91 (m, 2H). [Lit.[137] ^{1}H NMR ($CDCl_3$) δ 7.51 (s, 1H), δ 2.92 (m, 4H)]. ^{13}C NMR: ($CDCl_3$) (^{1}H decoupled) δ 197.2,

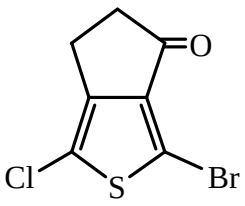


149.9, 143.8, 122.2, 122.0, 43.0, 20.8. Anal. Calcd. for C_7H_5OSCl: C 48.70; H 2.92. Found: C 48.51; H 2.98.

1-Bromo-3-chloro-5,6-dihydrocyclopenta[*c*]thiophen-4-one (147). To a solution of 3-chloro-5,6-dihydrorocyclopenta[*c*]thiophen-4-one (**145**) (0.26 g, 1.5 mmol) in 2 mL of dry DMF was added N-bromosuccinimide (NBS) (0.5 g, 2.8 mmol). The mixture was heated for three days at 85 °C. After cooling to room temperature the mixture was passed through a filter syringe (0.2 μM), then washed with saturated $NaHCO_3$ (2 x 10 mL), saturated NaCl (2 x 10 mL) and water (2 x 10 mL) and then dried over $MgSO_4$. The solvent was removed and the product mixture was subjected to flash chromatography using hexane:EtOAc (9:3). Compound **147** was obtained 87% yield (0.33 g) as a white solid, mp 77-79 °C. ^{1}H NMR ($CDCl_3$) δ 2.94 (m, 2H), 2.72 (m, 2H). MS [EI]; 250 (M^+), 252 (M^+ + 2), 254 (M^+ + 4), 222, 224, 226, 173 (M^+ − Br), 145. ^{13}C NMR: ($CDCl_3$) δ 195.4, 152.7, 139.5, 129.1, 101.3, 43.3, 21.6. IR (KBr, cm^{-1}) 3383, 2926, 2859, 1712, 1555, 1476, 1401, 1239, 1141, 1062, 983, 911, 813, 724, 656. Anal. Calcd. For $C_7H_4OSBrCl$: C, 33.43; H, 1.60. Found: C, 33.31; H, 1.51.

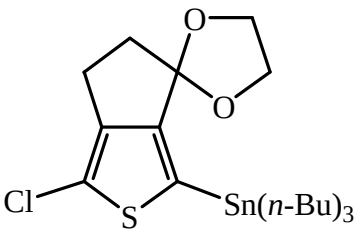


3-Bromo-1-chloro-5,6-dihydrocyclopenta[*c*]thiophen-4-one (148). To a solution of 1-chloro-5,6-dihydrorocyclopenta[*c*]thiophen-4-one (**145**) (0.26 g, 1.5 mmol) in 2 mL of dry DMF was added N-bromosuccinimide (NBS) (0.50 g, 2.8 mmol). The mixture was heated for three days at 85 °C. After cooling to room temperature the mixture was passed through a filter syringe (0.2 μM), then washed with saturated $NaHCO_3$ (2 x 10 mL), saturated NaCl (2 x



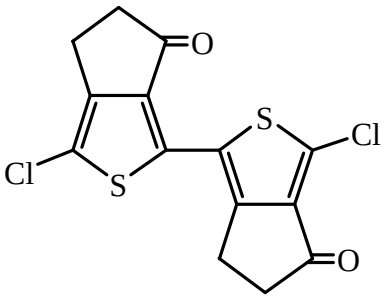
10 mL) and water (2 x 10 mL) and then dried over $MgSO_4$. The solvent was removed and the product mixture was subjected to flash chromatography, hexane:EtOAc (9:3). Compound **148** was prepared in 84% yield (0.32 g) and was obtained as a white solid, mp 92-94 °C. ^{1}H NMR ($CDCl_3$) δ 2.98 (m, 2H), 2.84 (m, 2H). ^{13}C NMR: ($CDCl_3$) (^{1}H decoupled) δ 195.8, 150.2, 141.5, 121.5, 108.5, 43.1, 20.3. MS [EI]; 250 (M^+), 252 (M^+ + 2), 254 (M^+ + 4), 222, 224, 226, 217 (M^+ − Cl), 189.0(M^+ − Cl − CO), 143.1, 108.1. IR (KBr, cm^{-1}) 3386, 2928, 2863, 1702, 1555, 1470, 1401, 1365, 1236, 1135, 1065, 980, 914, 818, 733, 652. Anal. Calcd. For $C_7H_4OSBrCl$: C, 33.43; H, 1.60. Found: C, 33.35; H, 1.31.

Spiro[1,3-dioxalane]-2,4'-1'-chloro,3'-tri-*n*-butylstannyl-5',6'-dihydro-



cyclopenta[*c*]thiophene (150). Compound **150** was prepared in similar manner to **80** and used in next step without further purification.

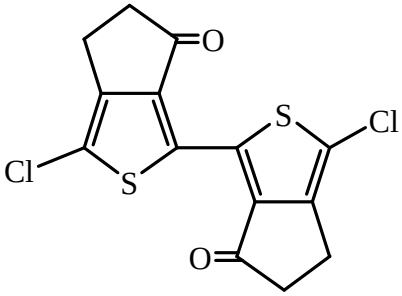
3,3'-Dichloro-4,4',5,5'-tetrahydro-1,1'-bi(cyclopenta[*c*]thiophene)-4,6'-dione (151).



1-Bromo-3-chloro-5,6-dihydrocyclopenta[*c*]thiophen-4-one (**148**) (50.0 mg, 0.20 mmol) and spiro[1,3-dioxalane]-2,4'-1'-chloro,3'-tri-*n*-butylstannyl-5',6'-dihydro-cyclopenta[*c*]thiophene (**150**) (150.0 mg, 0.30 mmol) was dissolved in 3 mL of dry DMF. Copper(I) iodide (3.8 mg, 0.02 mmol), triphenylphosphine (21 mg, 0.08 mmol) and $Pd_2(dba)_3$ (18.3 mg, 0.02 mmol) was added and the mixture which was heated at 80 ˚C for 24 h. The mixture was cooled to room temperature, filtered and subjected to flash chromatography

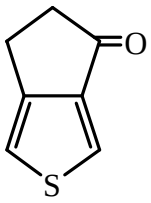
50% ethyl acetate / hexane to give compound **151** which was obtained in 18 % yield (12.4 mg, crude) as a green solid. The product was obtained as a mixture of compounds and was not fully characterized. MS [EI]; 342.1 (M^+), 344.1 (M^+ + 2), 256.1 (M^+ + 4), 313.0, 279.1, 237.0, 216.1, 171.1.

3,3'-Dichloro-4,4',5,5'-tetrahydro-1,1'-bi(cyclopenta[*c*]thiophene)-6,6'-dione (152).



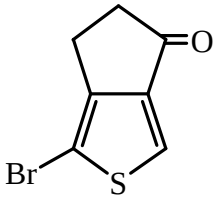
3-Bromo-3-chloro-5,6-dihydrocyclopenta[*c*]thiophen-4-one (**147**) (50.0 mg, 0.20 mmol) and spiro[1,3-dioxalane-2,4'-1'-chloro,3'-tri-*n*-butylstannyl-5',6'-dihydro-cyclopenta[*c*]thiophene] (**150**) (150.0 mg, 0.30 mmol) was dissolved in 3 mL of dry DMF. Copper(I) iodide (3.8 mg, 0.02 mmol), triphenylphosphine (21 mg, 0.08 mmol) and $Pd_2(dba)_3$ (18.3 mg, 0.02 mmol) was added and the mixture which was heated at 80 ˚C for 24 h. The mixture was cooled to room temperature, filtered and subjected to flash chromatography 50% ethyl acetate / hexane to give compound **151** which was obtained in 26 % yield (17.0 mg, crude) as a green solid. The product was obtained as a mixture of compounds and was not fully characterized. MS [EI]; 342.1 (M^+), 344.1 (M^+ + 2), 256.1 (M^+ + 4), 313.1, 279.2, 237.1, 216.3, 171.1.

5,6-Dihydrocyclopenta[*c*]thiophen-4-one (126).[134] A mixture of 1,3-dichloro-5,6-dihydrocyclopenta[*c*]thiophen-4-one (**132**) (5.0 g, 0.024 mol) and zinc (20g, 0.3 g-atom, 30 mesh granules) was suspended in water (95 mL) and glacial acetic acid (5 mL). The mixture was refluxed for 24 hours, cooled to room temperature and poured into ice. The product was extracted with



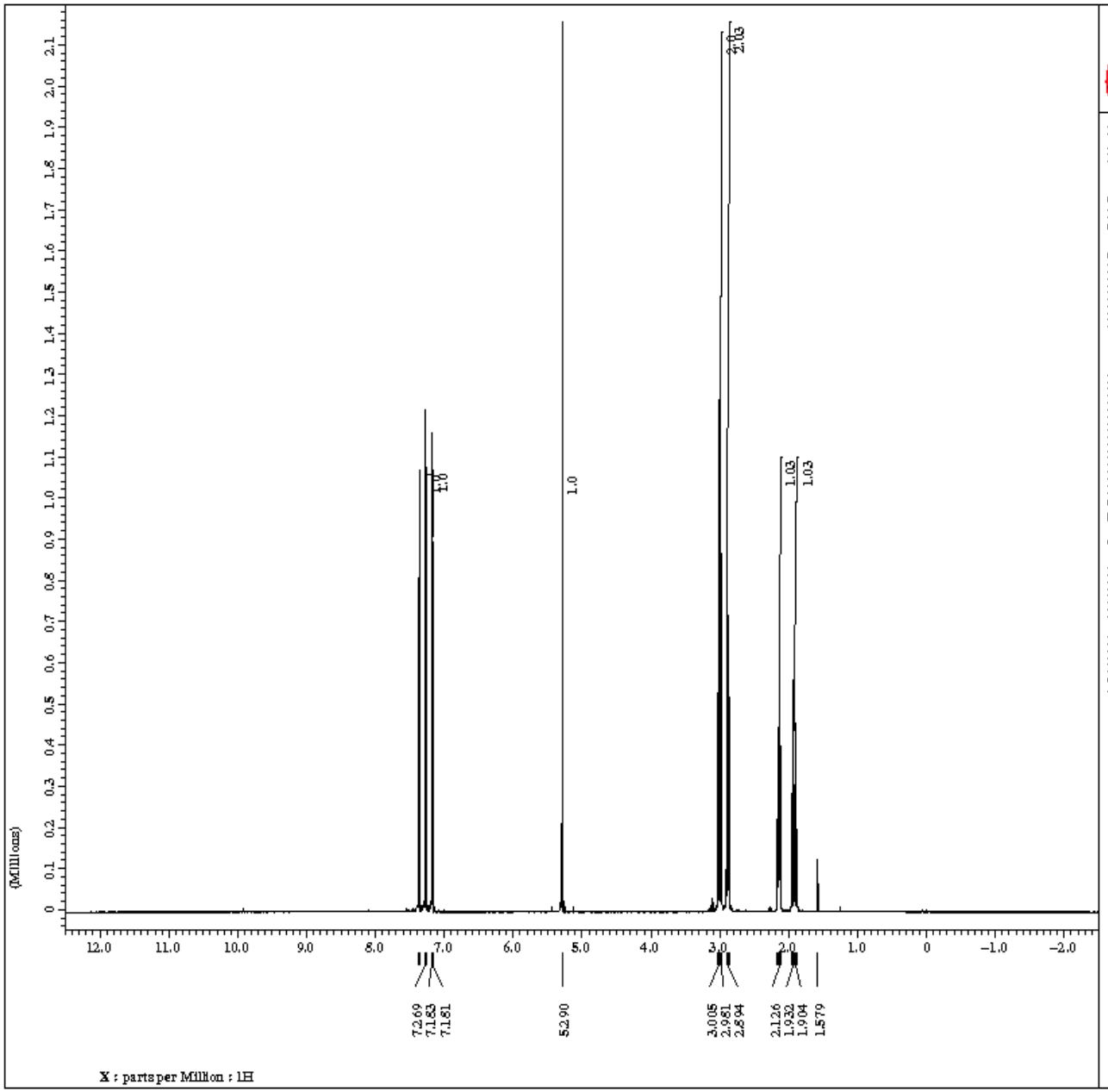
dichloromethane (5 x 100 mL) dried ($MgSO_4$), then the solvent was removed and the crude product was subjected to flash chromatography using ethyl acetate:hexane (2:5). The product was recrystallized from hexane and was obtained in 34% (1.13 g) as a white solid, mp mp 80-82°C (lit.[134] 81-82 °C). ^{1}H NMR ($CDCl_3$) δ 7.81 (d, *J* = 2.4, 1H), 7.01 (m, 1H), 3.00 (bs, 4H). [lit.[134] ^{1}H NMR ($CDCl_3$) δ 7.64 (d, *J* = 2.5, 1H), 7.01 (d, *J* = 2.5, 1H), 3.00 (s, 4H)]. ^{13}C NMR: ($CDCl_3$) (^{1}H decoupled) δ 197.9, 154.1, 144.4, 124.0, 117.1, 43.2, 21.7.

1-Bromo-5,6-dihydrocyclopenta[*c*]thiophen-4-one (153). To a solution of 5,6-dihydrorocyclopenta[*c*]thiophen-4-one (**126**) (0.56 g, 4.0 mmol) in 3 mL of dry DMF was added N-bromosuccinimide (NBS) (0.75 g, 4.2 mmol). The mixture was heated for three days at 85 °C. After cooling to room temperature the mixture was passed through a filter syringe (0.2 μM), then washed with saturated $NaHCO_3$ (2 x 10 mL), saturated NaCl (2 x 10 mL) and water (2 x 10 mL) and then dried over $MgSO_4$. The solvent was removed by rotary evaporation and the product mixture was subjected to flash chromatography using hexane:EtOAc (9:3).Compound **153** was prepared in 89% yield (077 g) and was obtained as a white solid, mp 103-105 °C. ^{1}H NMR ($CDCl_3$) δ 7.74 (s, 1H), 3.02 (m, 2H), 2.85 (m, 2H). ^{13}C NMR: ($CDCl_3$) (^{1}H decoupled) δ 197.2, 153.4, 144.5, 125.1, 104.8, 43.1, 21.6. MS [EI]; 216 (M^+), 218 (M^+ + 2), 190 (M^+ − CO), 137 (M^+ − Br), 109. IR (KBr, cm^{-1}) 3380, 3107, 2938, 2925, 2860, 1736, 1702, 1551, 1465, 1437, 1394, 1282, 1239, 1171, 1118, 1019, 988, 973, 924, 854, 814, 773, 698, 613. Anal. Calcd. For C_7H_5OSBr: C, 38.73; H, 2.32. Found: C, 38.41; H, 2.19.



APPENDIX 1

^{1}H, ^{13}C NMR and IR spectra of 2-thiophene-3-yl-(1,3)dithiane (**70**)



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Creation_time = 15-NOV-2008 04:31:55
Revision_time = 8-DEC-2008 17:27:02
Current_time = 8-DEC-2008 17:36:07

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Spectrometer = DELTA_NMR

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X_offset = 5[ppm]
X_points = 131072
X_prescans = 0
X_resolution = 57.27773672[mHz]
X_sweep = 7.50750751[kHz]
Clipped = FALSE
Mod_return = 1
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Total_scans = 15

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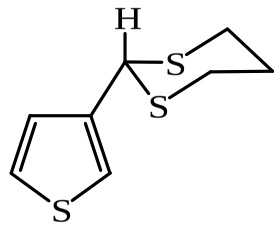
X_acq_time = 17.458790&[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 15
Relaxation_delay = 30[s]
Temp_get = 26.1[dC]
Unblank_time = 2[us]



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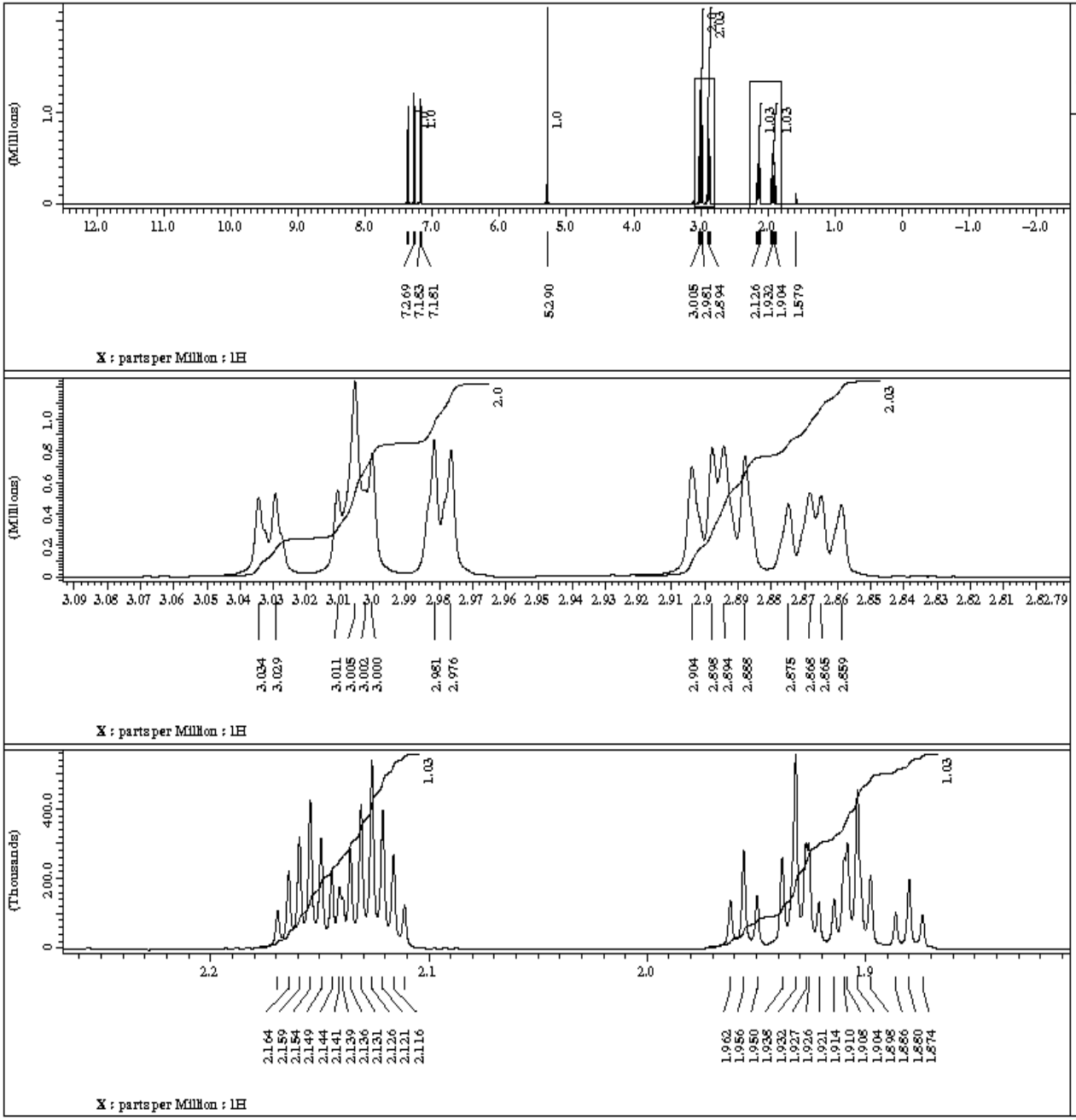

JEOL

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Spectrometer      = DELTA_NMR

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X_sweep           = 7.50750751[kHz]
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Mod_return        = 1
Scans             = 15
Total_scans       = 15

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X_angle           = 45[deg]
X_pulse           = 9.25[us]
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Recvr_gain        = 15
Relaxation_delay  = 30[s]
Temp_get          = 26.1[dC]
Unblank_time      = 2[us]
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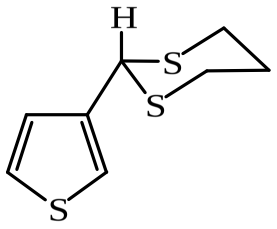

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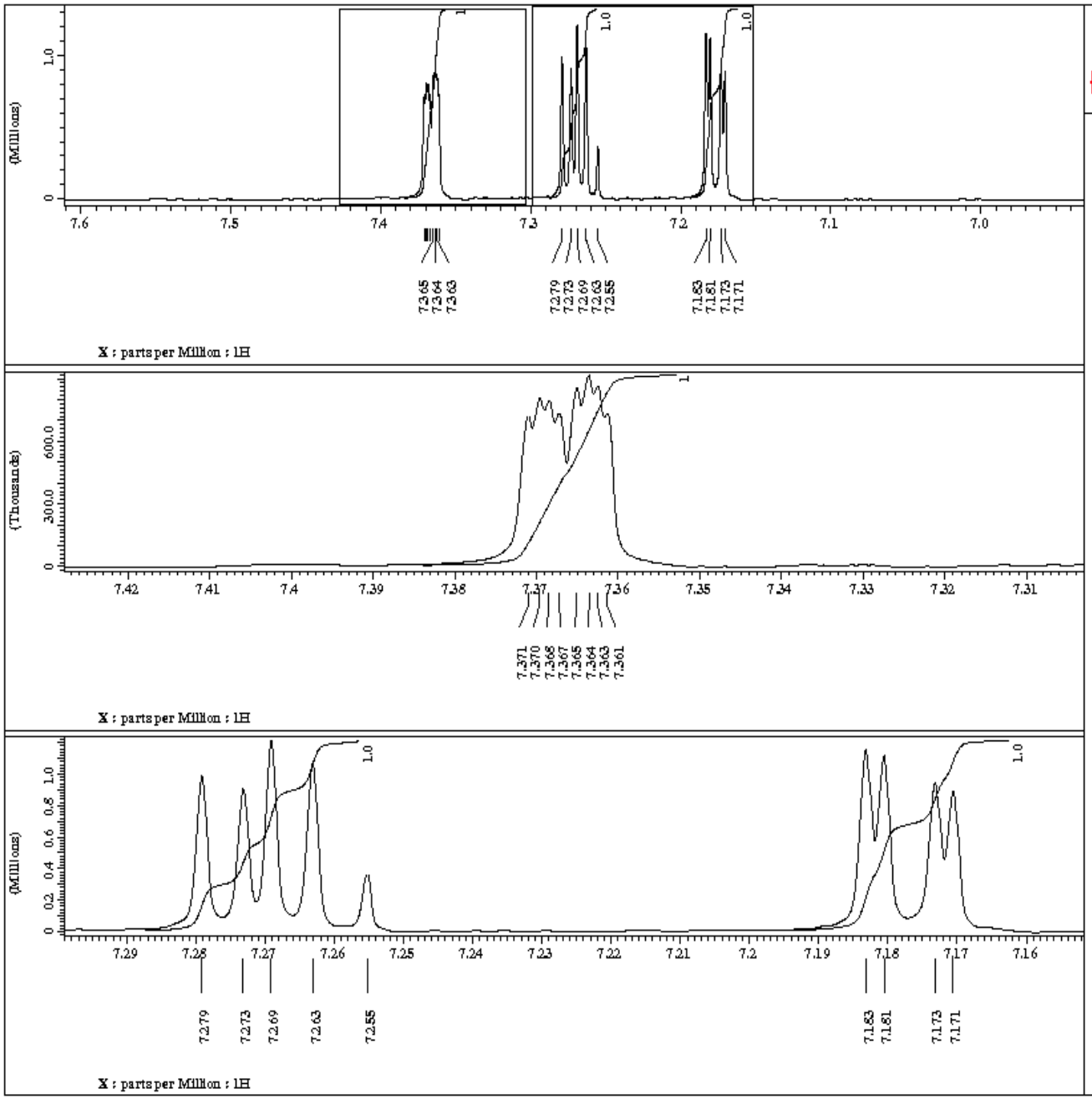

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Revision_time     =  8-DEC-2008 17:27:02
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Spectrometer      = DELTA_NMR

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X_offset          = 5[ppm]
X_points          = 131072
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X_resolution      = 57.27773672[mHz]
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Clipped           = FALSE
Mod_return        = 1
Scans             = 15
Total_scans       = 15

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X_acq_time        = 17.4587904[s]
X_angle           = 45[deg]
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Phase_preset      = 3[us]
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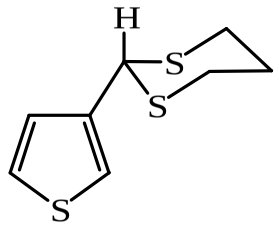

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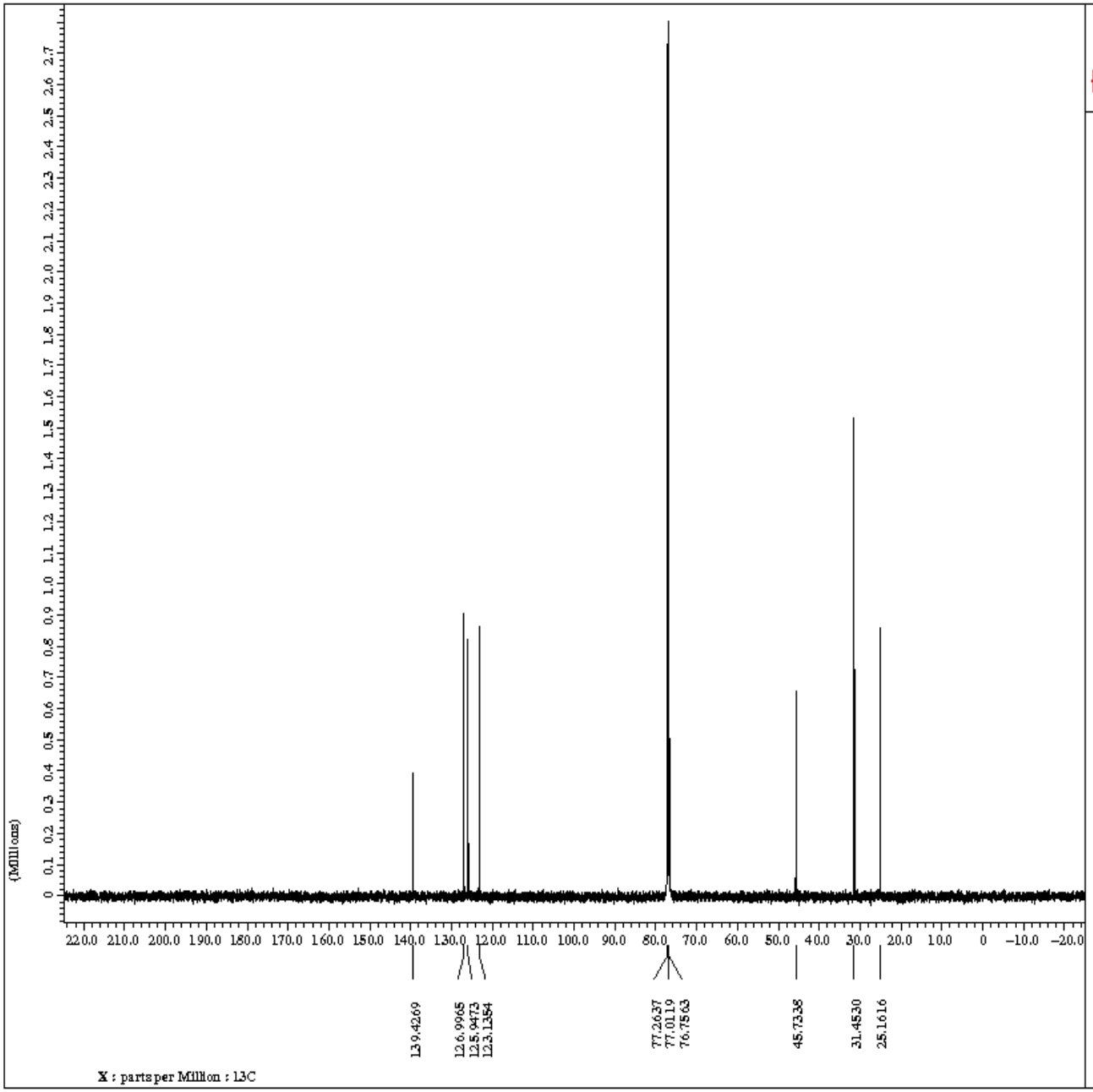
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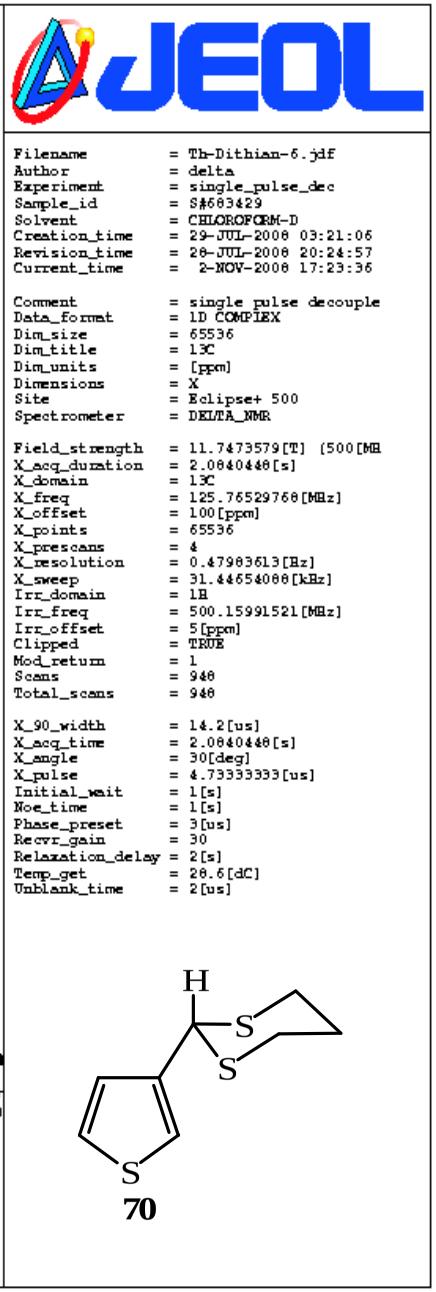
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 −10.0 −20.0
139.4269
126.9965
125.9473
123.1354
77.2637
77.0119
76.7563
45.7338
31.4530
25.1616
X : parts per Million : 13C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Sample_id = S#603429
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Revision_time = 28-JUL-2008 20:24:57
Current_time = 2-NOV-2008 17:23:36
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X_sweep = 31.44654088[kHz]
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Irr_freq = 500.15991521[MHz]
Irr_offset = 5[ppm]
Clipped = TRUE
Mod_return = 1
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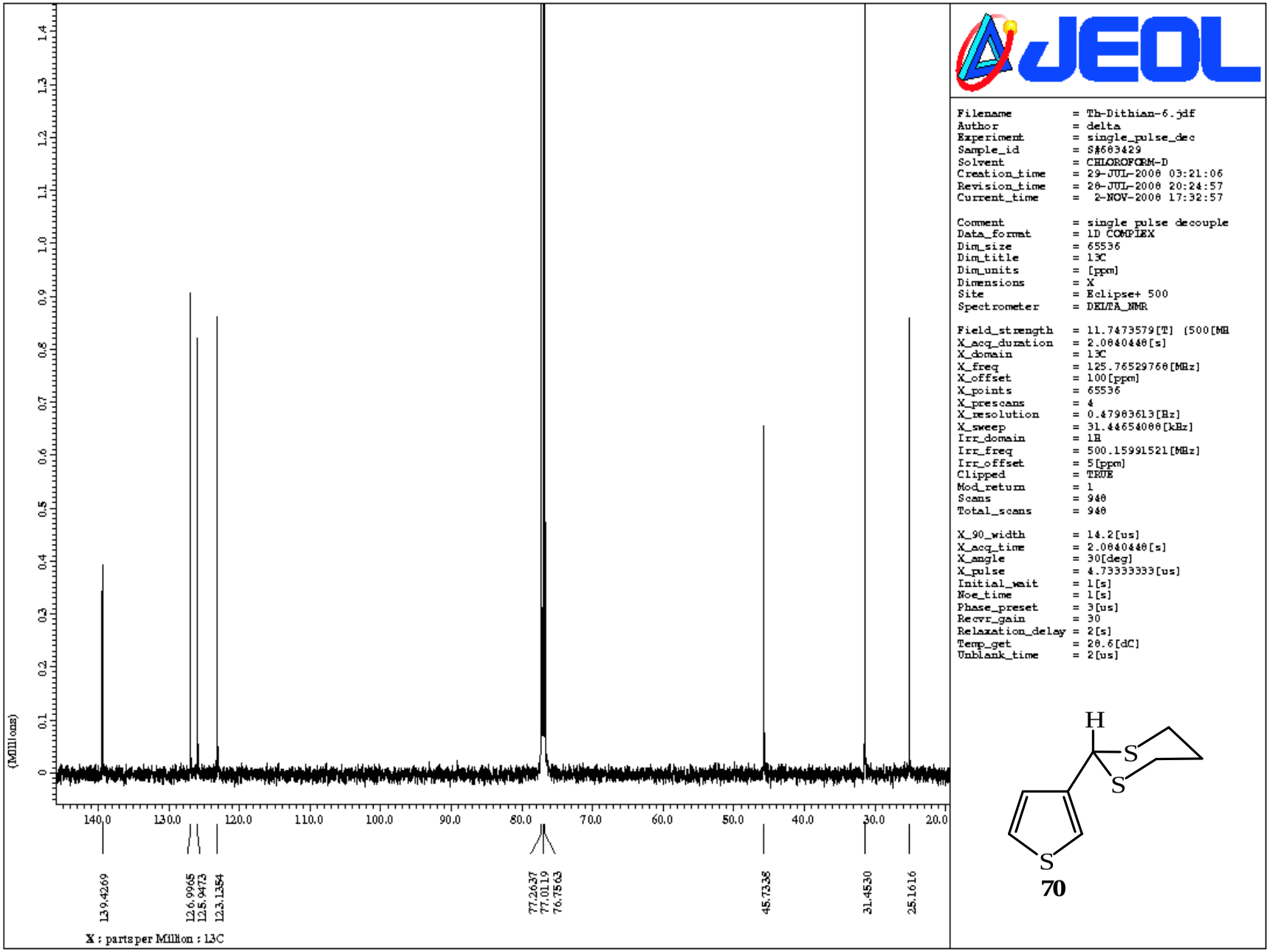
S
S
S

70



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X_offset          = 100[ppm]
X_points          = 65536
X_prescans        = 4
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X_sweep           = 31.44654088[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5[ppm]
Clipped           = TRUE
Mod_return        = 1
Scans             = 948
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X_pulse           = 4.73333333[us]
Initial_wait      = 1[s]
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Phase_preset      = 3[us]
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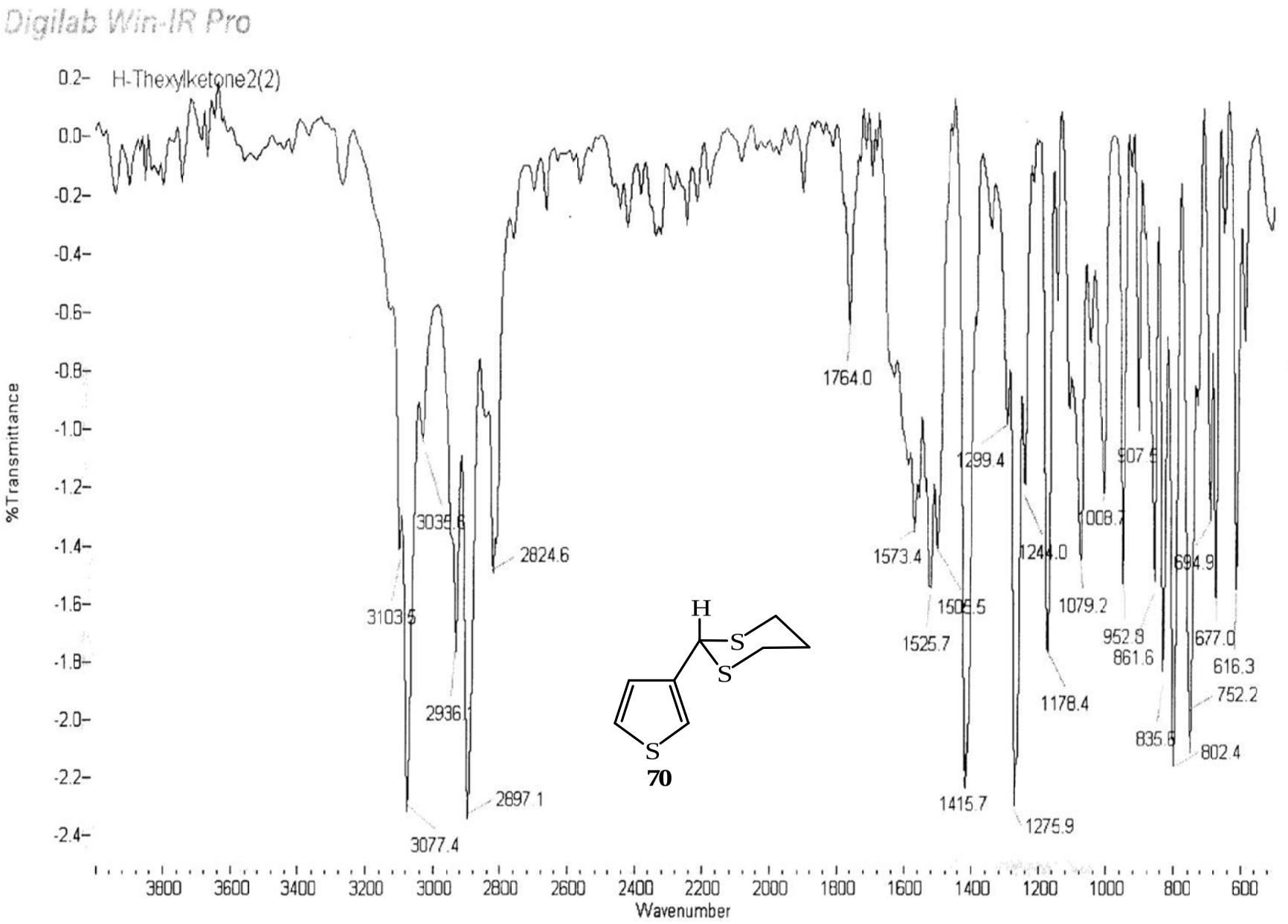
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616.3
802.4
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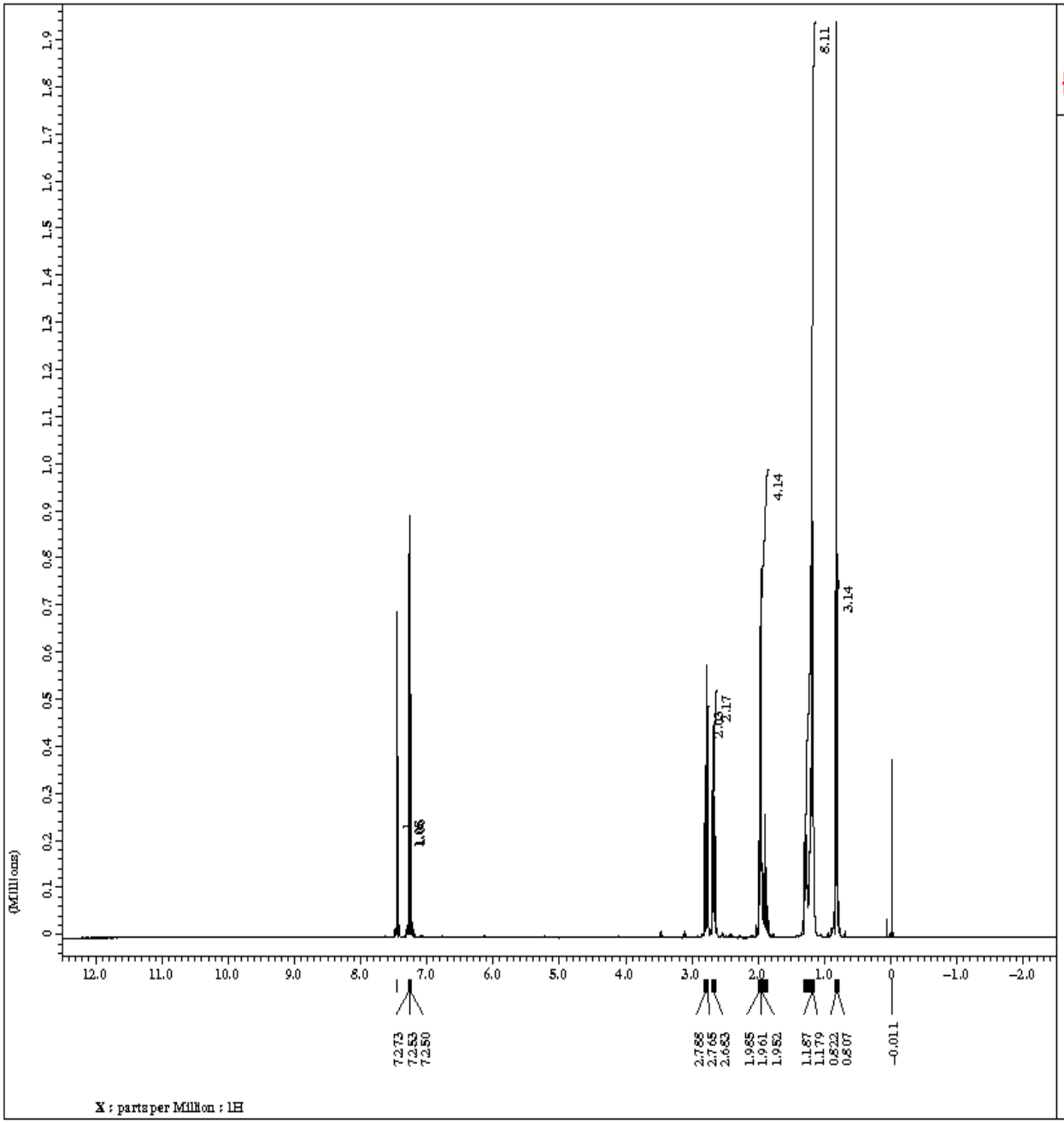
70

APPENDIX 2

^{1}H, ^{13}C NMR and IR spectra of 2-hexyl-2-thiophene-3-yl-(1,3)dithiane (**71**)



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Revision_time = 8-DEC-2008 17:58:33
Current_time = 8-DEC-2008 18:38:39

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X_resolution = 57.27773672[mHz]
X_sweep = 7.50750751[kHz]
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X_acq_time = 17.4587904[s]
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X_pulse = 9.25[us]
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Relaxation_delay = 30[s]
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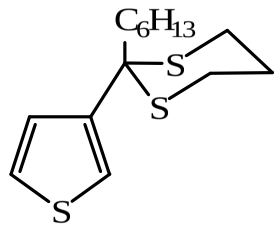

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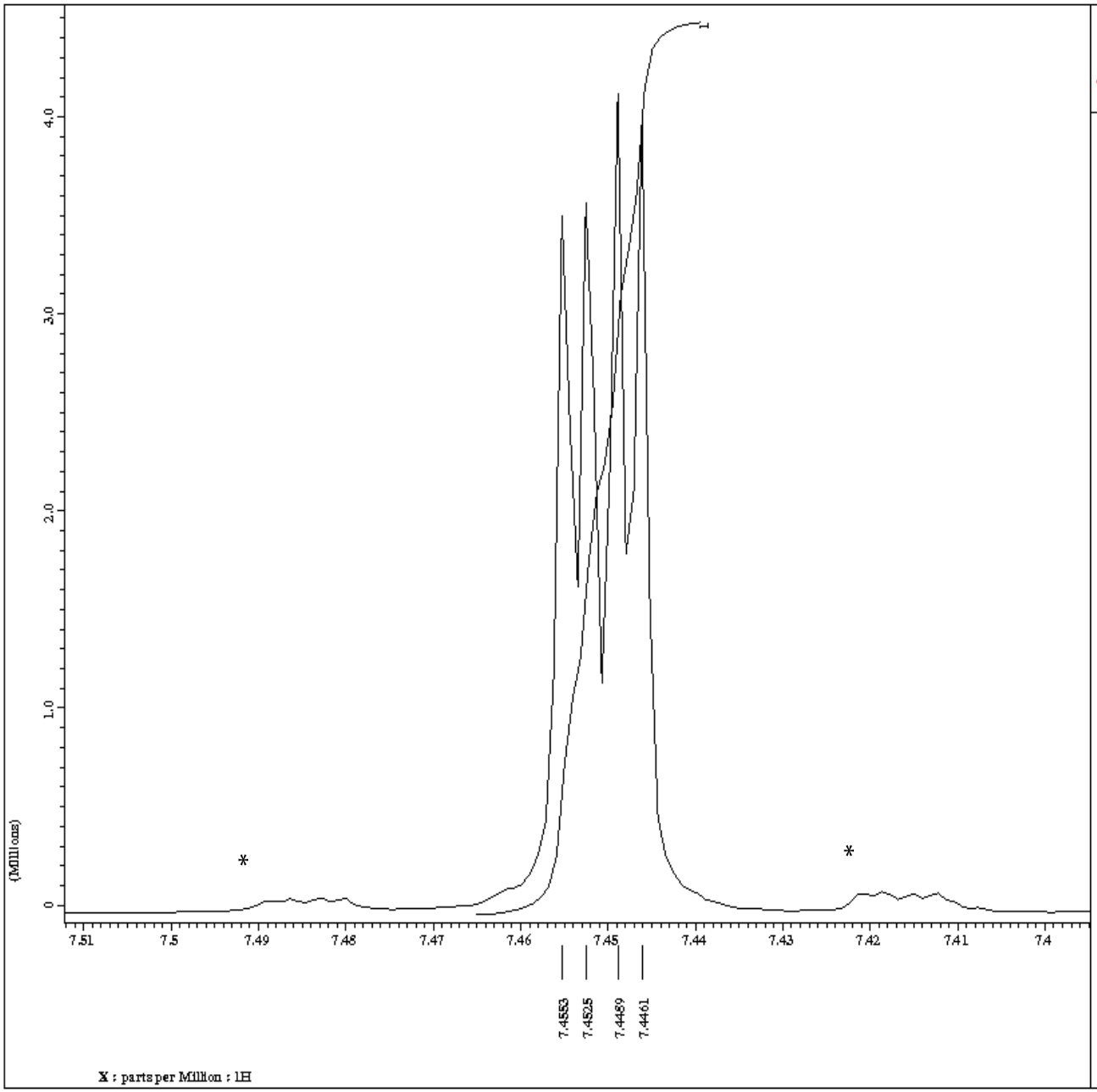

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Current_time	= 3-NOV-2008 21:36:15
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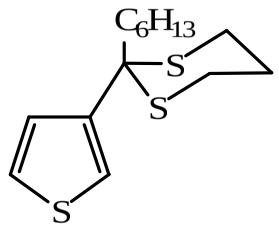

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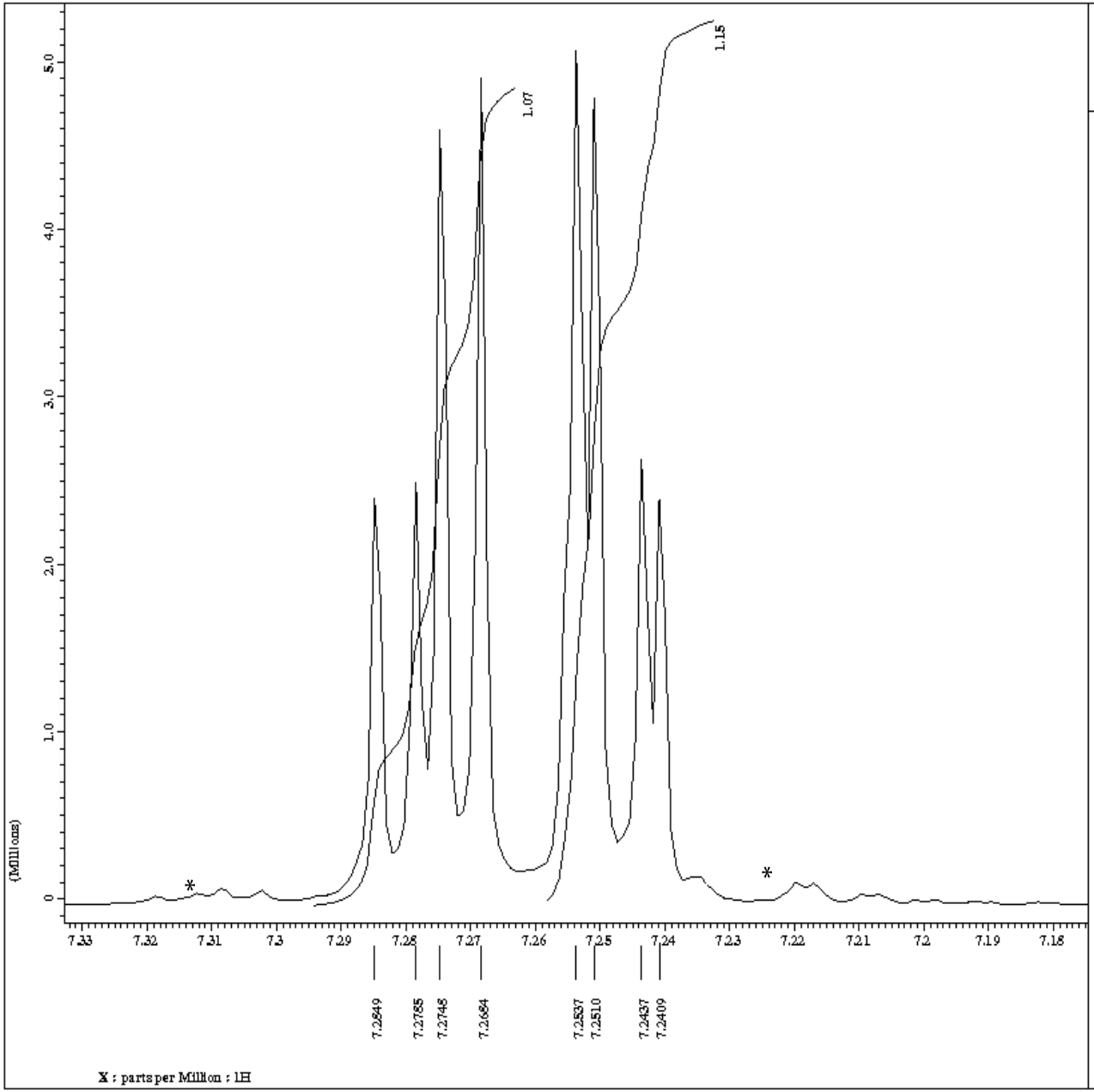

JEOL

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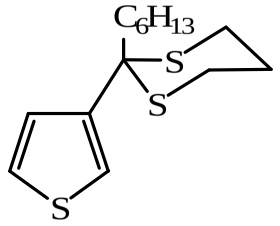
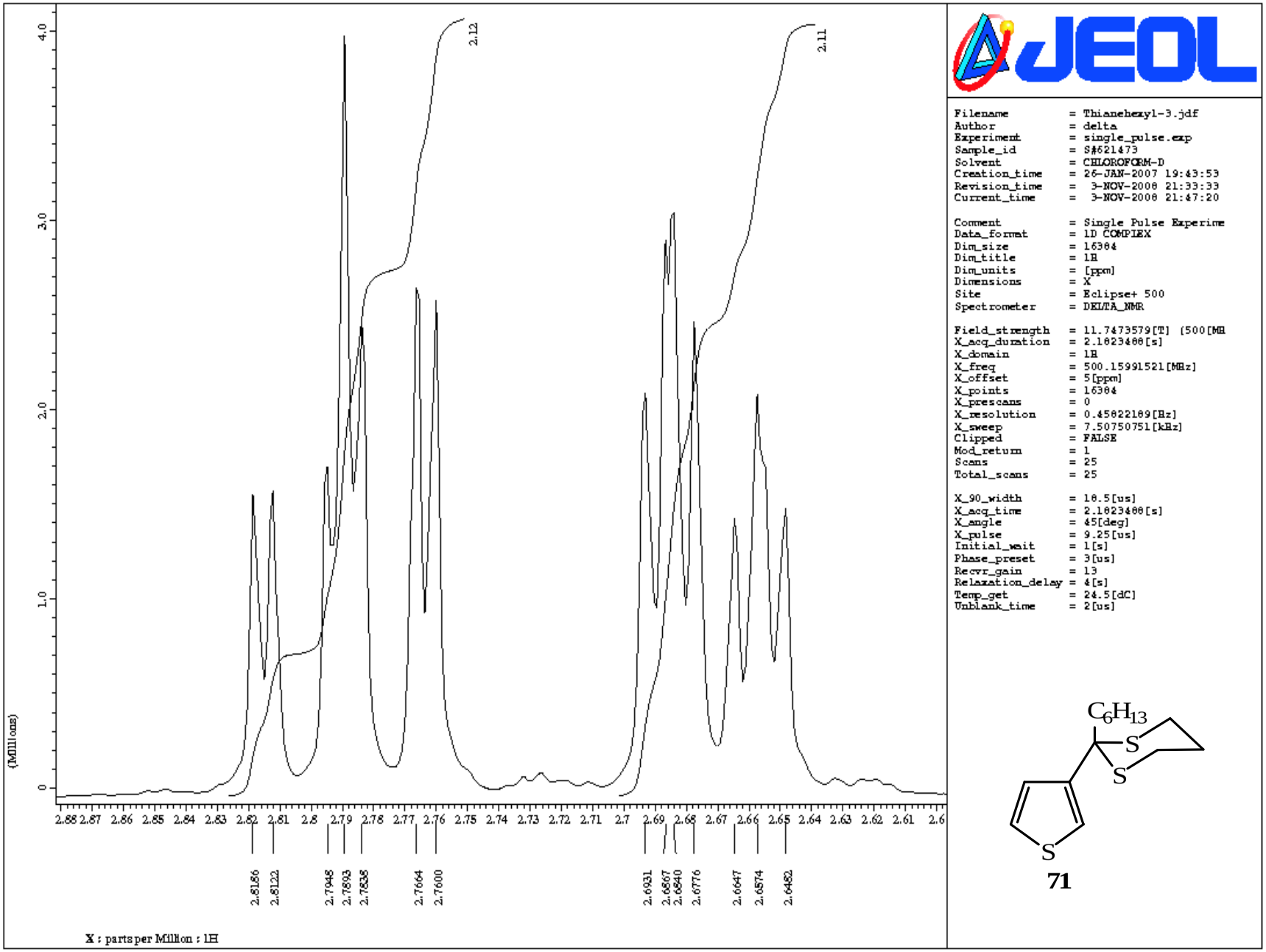
X_resolution      = 0.45822189[Hz]
X_sweep           = 7.50750751[kHz]
Clipped           = FALSE
Mod_return        = 1
Scans             = 25
Total_scans       = 25

X_90_width        = 10.5[us]
X_acq_time        = 2.1823488[s]
X_angle           = 45[deg]
X_pulse           = 9.25[us]
Initial_wait      = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 13
Relaxation_delay  = 4[s]
Temp_get          = 24.5[dC]
Unblank_time      = 2[us]
```



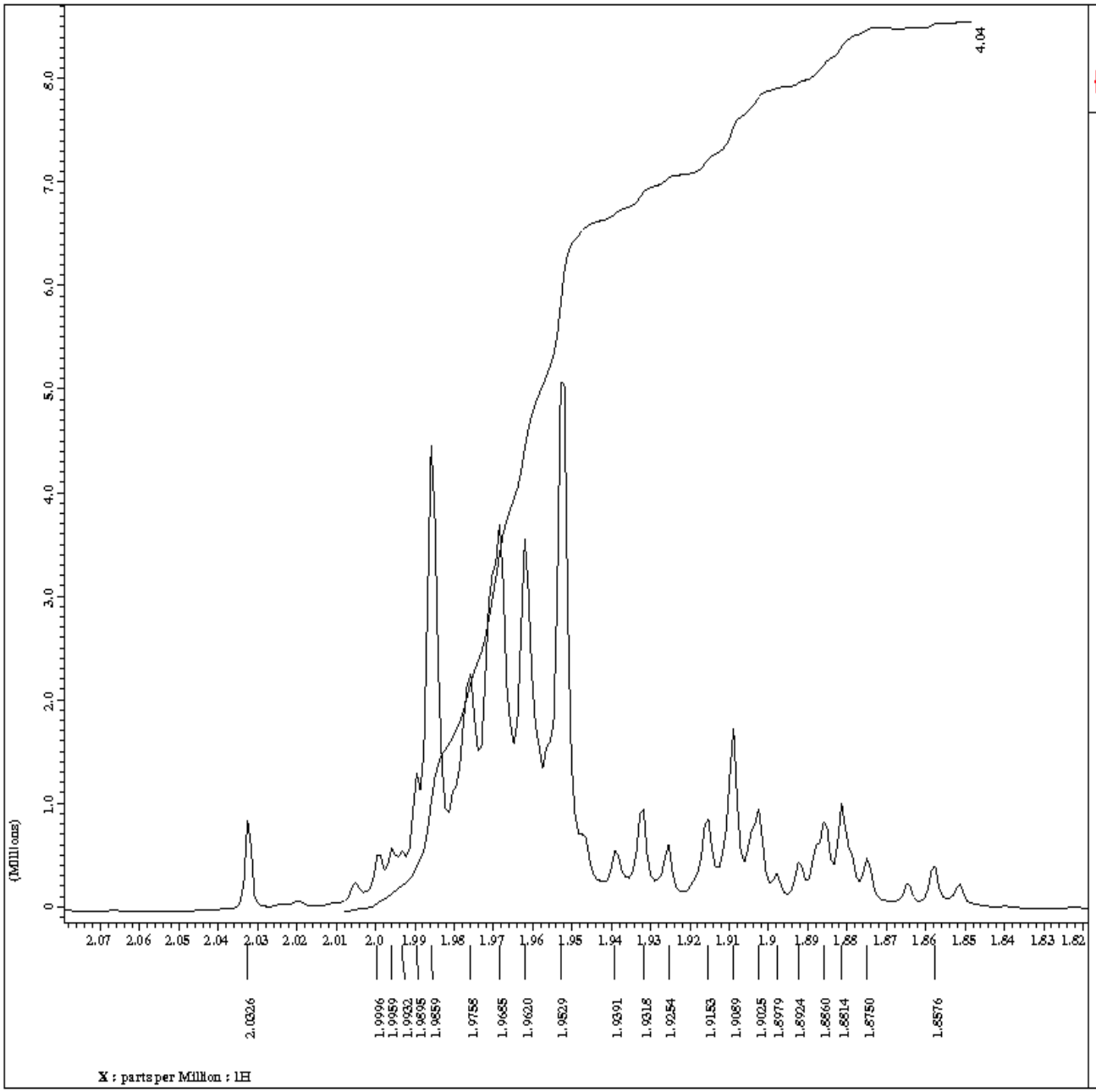
71

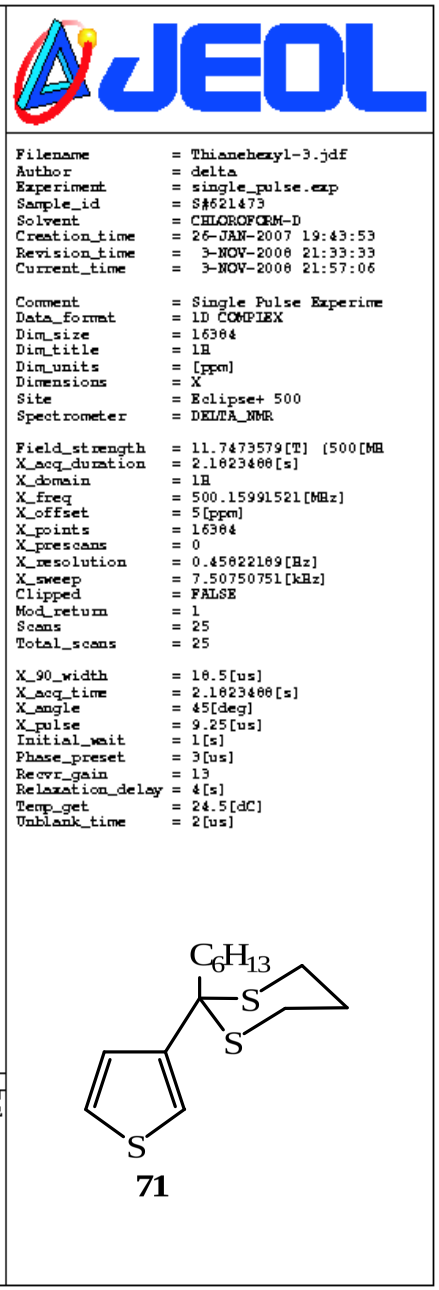


JEOL

Filename	= Thianehexyl-3.jdf
Author	= delta
Experiment	= single_pulse.exp
Sample_id	= S#621&73
Solvent	= CHLOROFORM-D
Creation_time	= 26-JAN-2007 19:43:53
Revision_time	= 3-NOV-2006 21:33:33
Current_time	= 3-NOV-2006 21:47:20
Comment	= Single Pulse Experime
Data_format	= 1D COMPLEX
Dim_size	= 16384
Dim_title	= 1H
Dim_units	= [ppm]
Dimensions	= X
Site	= Eclipse+ 500
Spectrometer	= DELTA_NMR
Field_strength	= 11.7473579[T] (500[MH
X_acq_duration	= 2.1823488[s]
X_domain	= 1H
X_freq	= 500.15991521[MHz]
X_offset	= 5[ppm]
X_points	= 16384
X_prescans	= 0
X_resolution	= 0.45822189[Hz]
X_sweep	= 7.50750751[kHz]
Clipped	= FALSE
Mod_return	= 1
Scans	= 25
Total_scans	= 25
X_90_width	= 10.5[us]
X_acq_time	= 2.1823488[s]
X_angle	= 45[deg]
X_pulse	= 9.25[us]
Initial_wait	= 1[s]
Phase_preset	= 3[us]
Recvr_gain	= 13
Relaxation_delay	= 4[s]
Temp_get	= 24.5[dC]
Unblank_time	= 2[us]

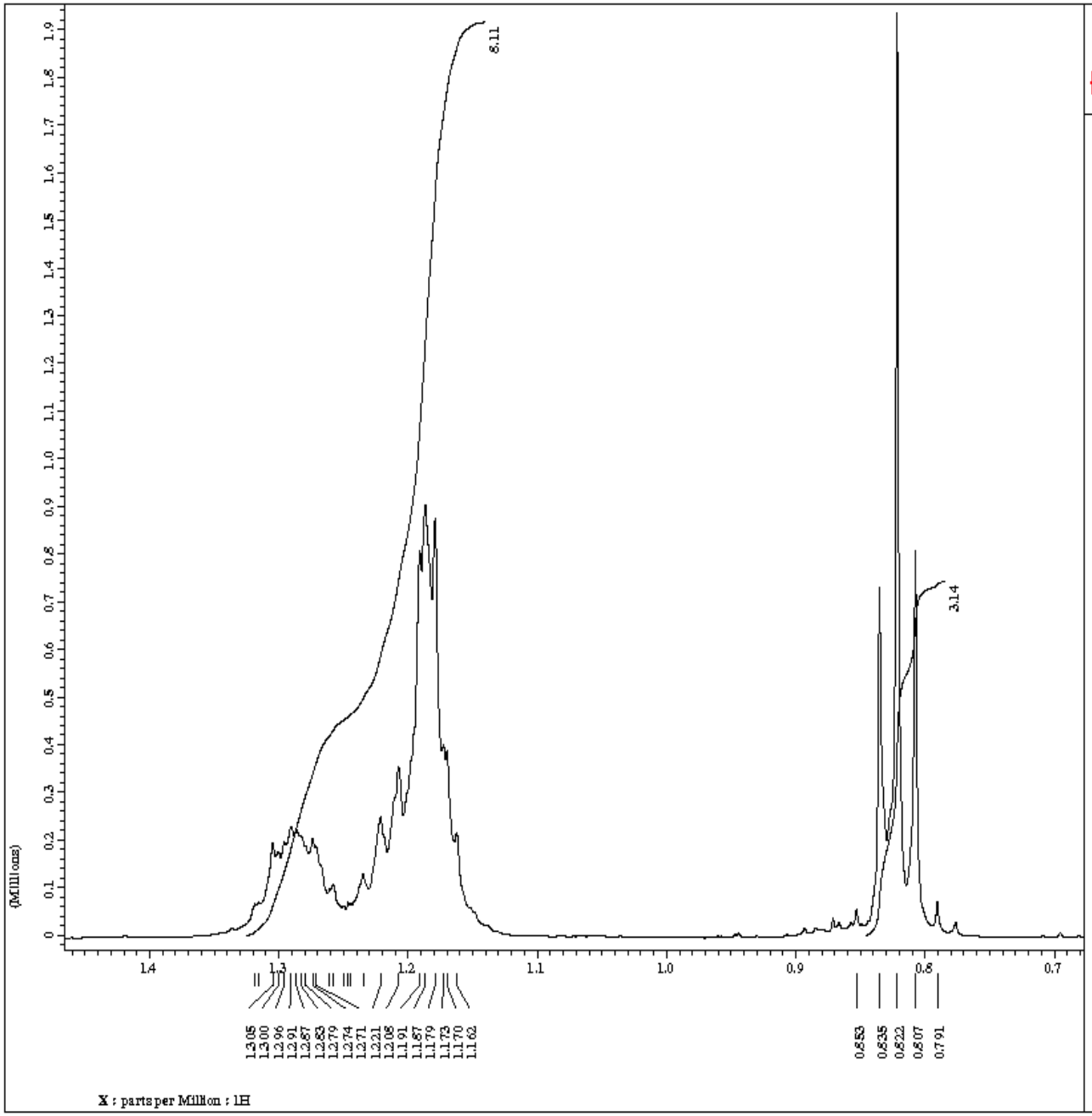
71


4.04
(Millions)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
2.07 2.06 2.05 2.04 2.03 2.02 2.01 2.0 1.99 1.98 1.97 1.96 1.95 1.94 1.93 1.92 1.91 1.9 1.89 1.88 1.87 1.86 1.85 1.84 1.83 1.82
2.03026
1.9996
1.9959
1.9932
1.9895
1.9859
1.9758
1.9685
1.9620
1.9529
1.9391
1.9318
1.9254
1.9153
1.9089
1.9025
1.8979
1.8924
1.8860
1.8814
1.8750
1.8576
X : parts per Million : 1H


JEOL
Filename = Thianehexyl-3.jdf
Author = delta
Experiment = single_pulse.exp
Sample_id = S#621473
Solvent = CHLOROFORM-D
Creation_time = 26-JAN-2007 19:43:53
Revision_time = 3-NOV-2008 21:33:33
Current_time = 3-NOV-2008 21:57:06
Comment = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1023488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Clipped = FALSE
Mod_return = 1
Scans = 25
Total_scans = 25
X_90_width = 10.5[us]
X_acq_time = 2.1023488[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 13
Relaxation_delay = 4[s]
Temp_get = 24.5[dC]
Unblank_time = 2[us]

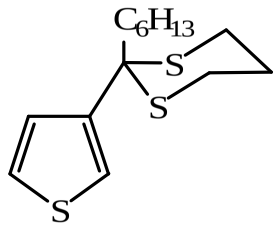
C6H13
S
S
S

71

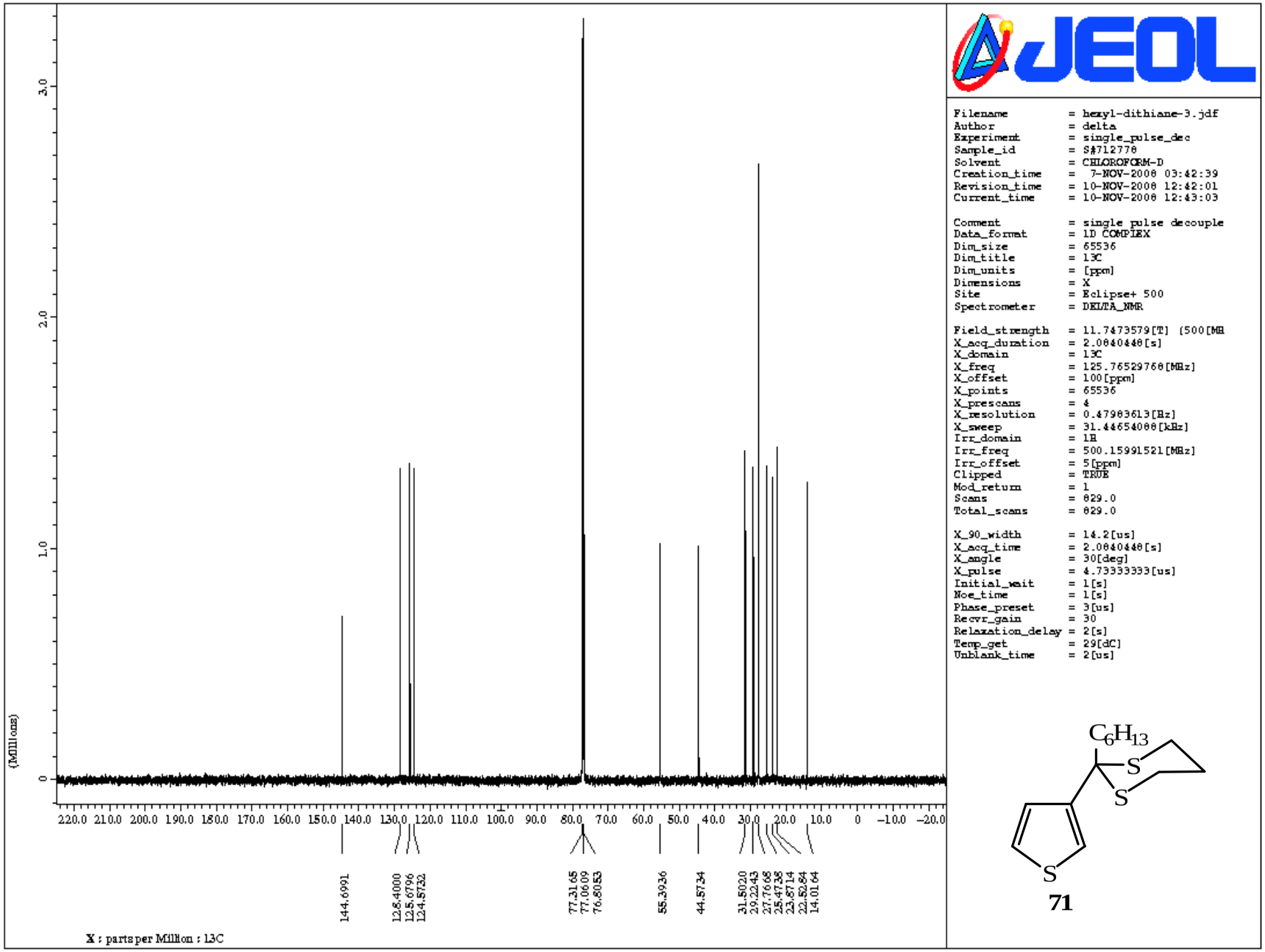


JEOL

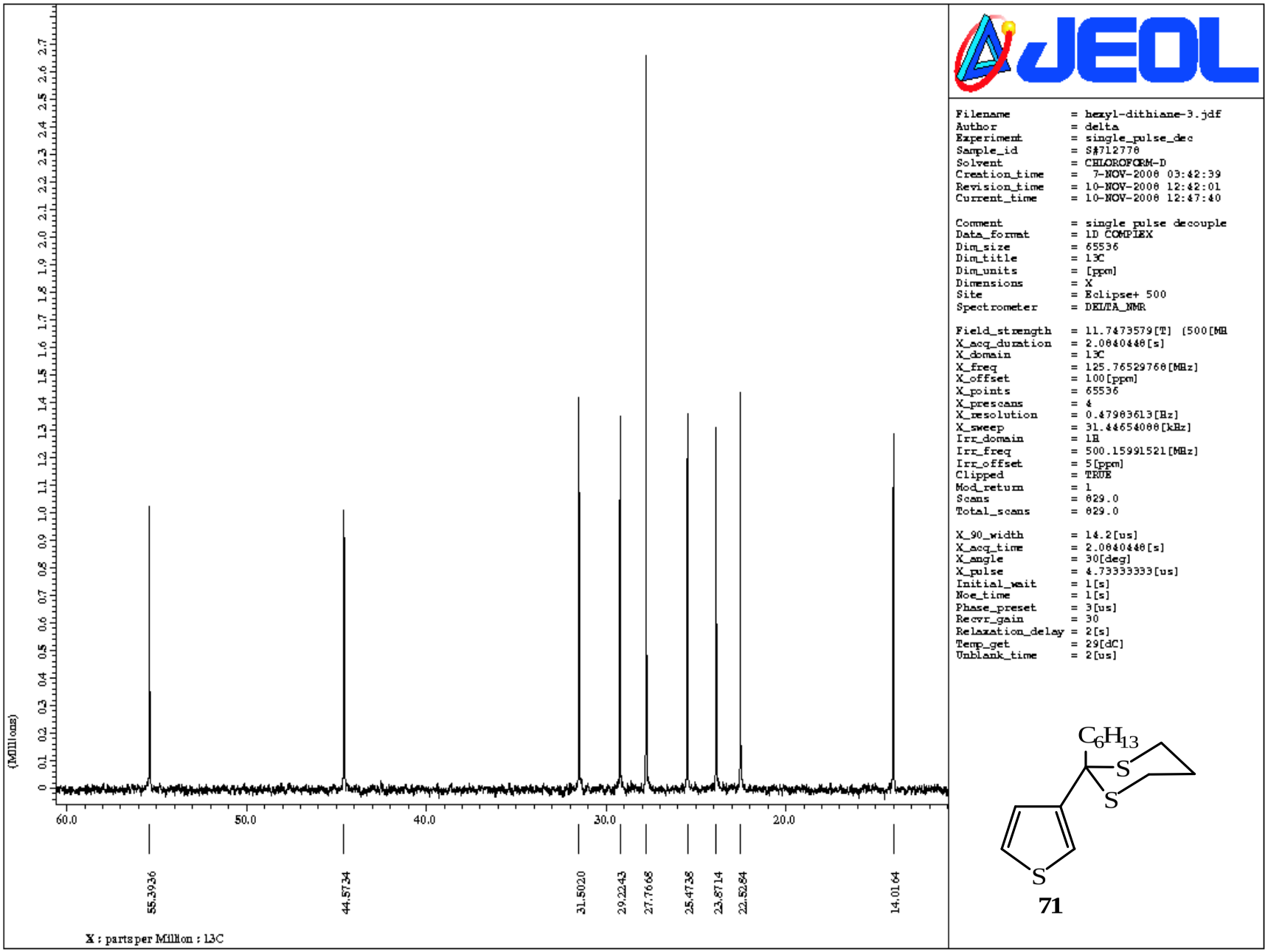
Filename	= Dithian-hexyl-thio-4.
Author	= delta
Experiment	= single_pulse.exp
Sample_id	= S#623516
Solvent	= CHLOROFORM-D
Creation_time	= 26-JAN-2007 20:00:10
Revision_time	= 6-DEC-2008 17:58:33
Current_time	= 6-DEC-2008 18:42:47
Comment	= Single Pulse Experime
Data_format	= 1D COMPLEX
Dim_size	= 131072
Dim_title	= 1H
Dim_units	= [ppm]
Dimensions	= X
Site	= Eclipse+ 500
Spectrometer	= DELTA_NMR
Field_strength	= 11.7473579[T] (500[MH
X_acq_duration	= 17.4587904[s]
X_domain	= 1H
X_freq	= 500.15991521[MHz]
X_offset	= 5[ppm]
X_points	= 131072
X_prescans	= 0
X_resolution	= 57.27773672[mHz]
X_sweep	= 7.50750751[kHz]
Clipped	= FALSE
Mod_return	= 1
Scans	= 14
Total_scans	= 14
X_90_width	= 18.5[us]
X_acq_time	= 17.4587904[s]
X_angle	= 45[deg]
X_pulse	= 9.25[us]
Initial_wait	= 1[s]
Phase_preset	= 3[us]
Recvr_gain	= 13
Relaxation_delay	= 30[s]
Temp_get	= 24.5[dC]
Unblank_time	= 2[us]



71


(Millions)
3.0
2.0
1.0
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 −10.0 −20.0
144.6991
128.4000
125.6796
124.8732
77.31.65
77.06.09
76.80.53
55.3936
44.8734
31.5020
29.2243
27.7668
25.4738
23.8714
22.5284
14.0164
X : parts per Million : 13C
Filename = hexyl-dithiane-3.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = S#712778
Solvent = CHLOROFORM-D
Creation_time = 7-NOV-2008 03:42:39
Revision_time = 10-NOV-2008 12:42:01
Current_time = 10-NOV-2008 12:43:03
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 65536
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.0840448[s]
X_domain = 13C
X_freq = 125.76529768[MHz]
X_offset = 100[ppm]
X_points = 65536
X_prescans = 4
X_resolution = 0.47983613[Hz]
X_sweep = 31.44654088[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5[ppm]
Clipped = TRUE
Mod_return = 1
Scans = 829.0
Total_scans = 829.0
X_90_width = 14.2[us]
X_acq_time = 2.0840448[s]
X_angle = 30[deg]
X_pulse = 4.73333333[us]
Initial_wait = 1[s]
Noe_time = 1[s]
Phase_preset = 3[us]
Recvr_gain = 30
Relaxation_delay = 2[s]
Temp_get = 29[dC]
Unblank_time = 2[us]
C6H13
S
S
S

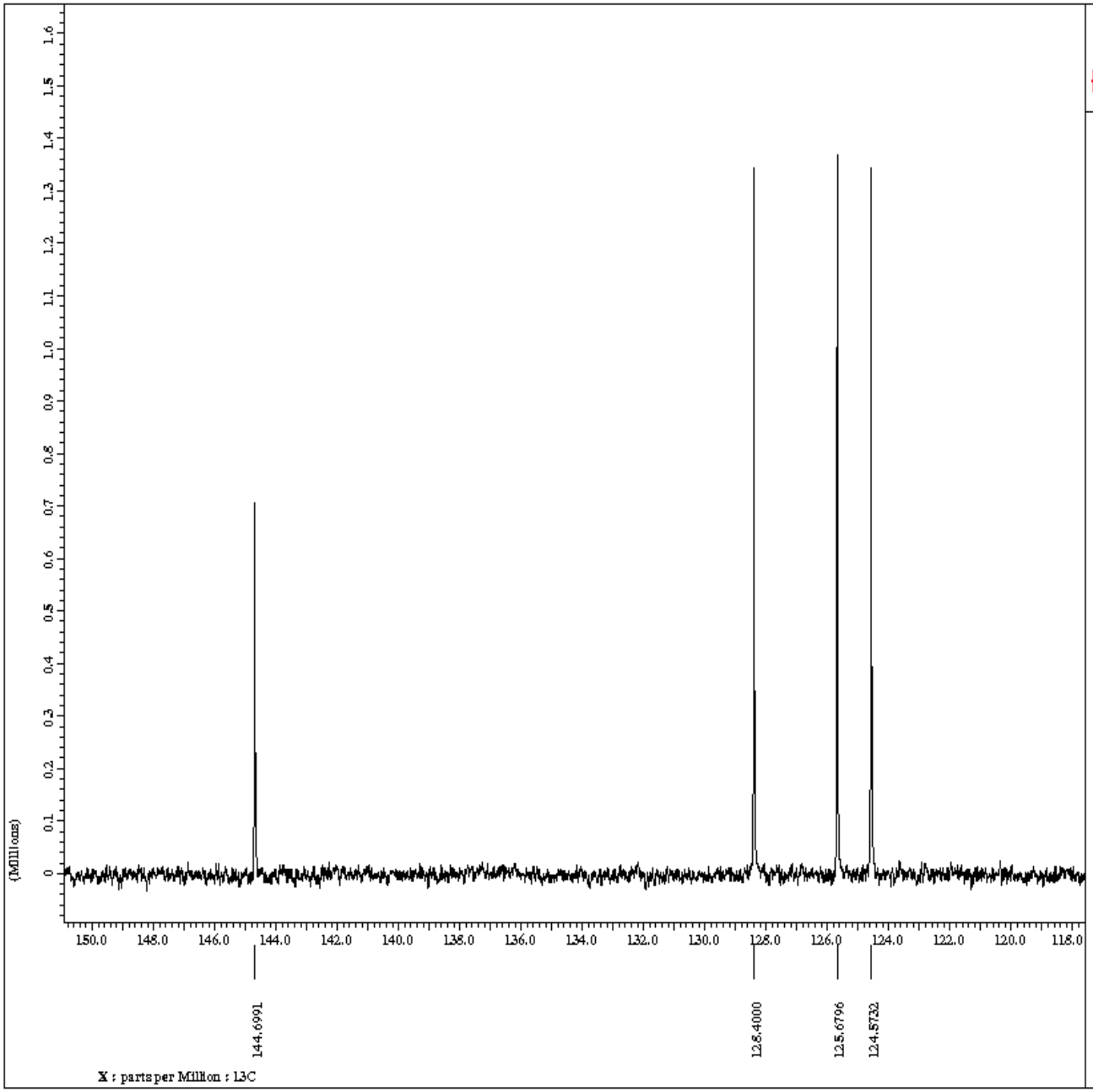
71



JEOL

Filename	= hexyl-dithiane-3.jdf
Author	= delta
Experiment	= single_pulse_dec
Sample_id	= S#712770
Solvent	= CHLOROFORM-D
Creation_time	= 7-NOV-2008 03:42:39
Revision_time	= 10-NOV-2008 12:42:01
Current_time	= 10-NOV-2008 12:47:40
Comment	= single pulse decouple
Data_format	= 1D COMPLEX
Dim_size	= 65536
Dim_title	= 13C
Dim_units	= [ppm]
Dimensions	= X
Site	= Eclipse+ 500
Spectrometer	= DELTA_NMR
Field_strength	= 11.7473579[T] (500[MH
X_acq_duration	= 2.0840448[s]
X_domain	= 13C
X_freq	= 125.76529768[MHz]
X_offset	= 100[ppm]
X_points	= 65536
X_prescans	= 4
X_resolution	= 0.47983613[Hz]
X_sweep	= 31.44654088[kHz]
Irr_domain	= 1H
Irr_freq	= 500.15991521[MHz]
Irr_offset	= 5[ppm]
Clipped	= TRUE
Mod_return	= 1
Scans	= 829.0
Total_scans	= 829.0
X_90_width	= 14.2[us]
X_acq_time	= 2.0840448[s]
X_angle	= 30[deg]
X_pulse	= 4.73333333[us]
Initial_wait	= 1[s]
Noe_time	= 1[s]
Phase_preset	= 3[us]
Recvr_gain	= 30
Relaxation_delay	= 2[s]
Temp_get	= 29[dC]
Unblank_time	= 2[us]

71



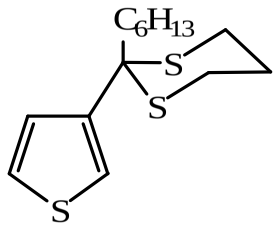
JEOL

```
Filename          = hexyl-dithiane-3.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#712770
Solvent           = CHLOROFORM-D
Creation_time     =  7-NOV-2008 03:42:39
Revision_time     = 10-NOV-2008 12:42:01
Current_time      = 10-NOV-2008 12:58:37

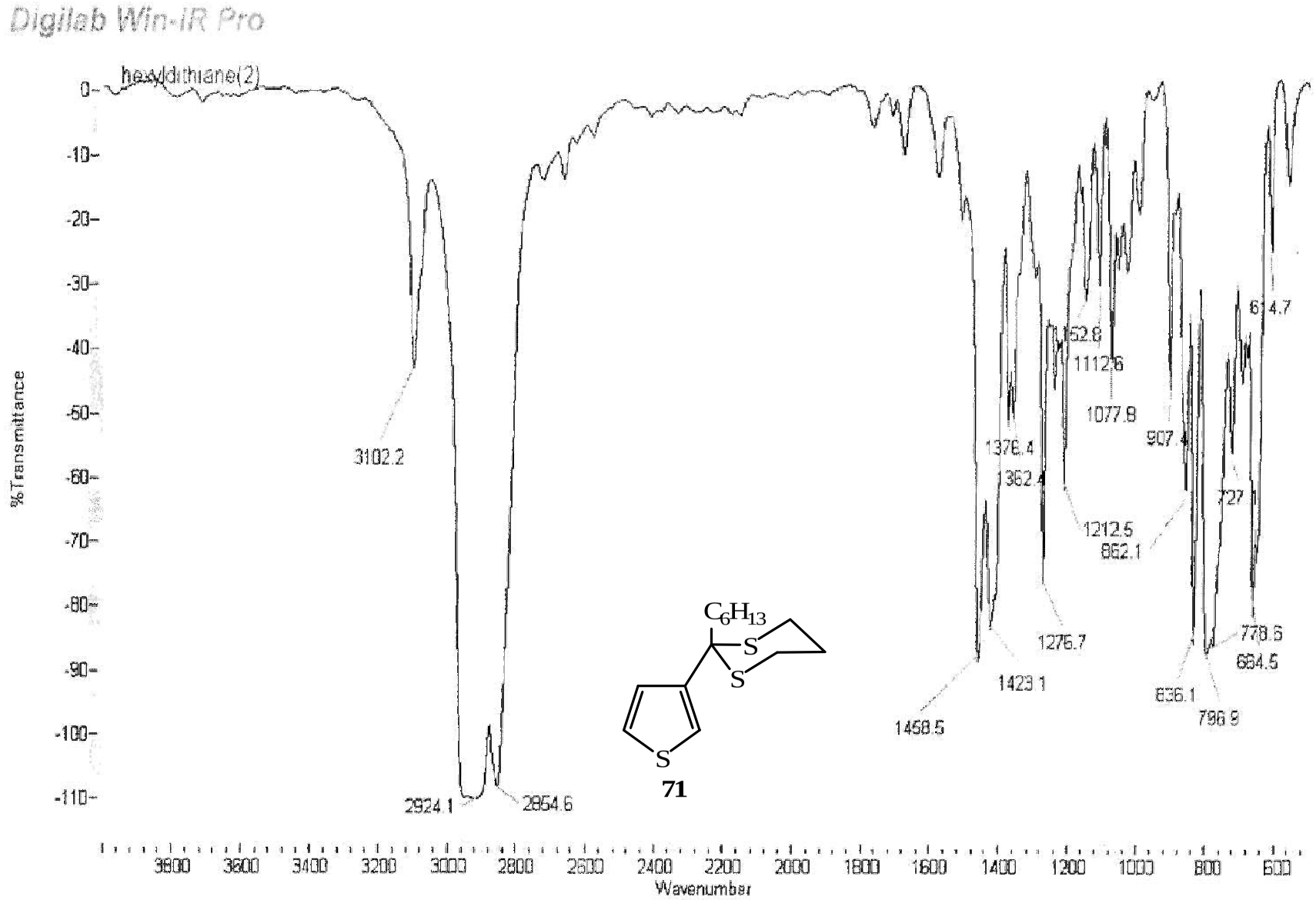
Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 65536
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

Field_strength    = 11.7473579[T]  (500[MH
X_acq_duration    = 2.0840448[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 65536
X_prescans        = 4
X_resolution      = 0.47983613[Hz]
X_sweep           = 31.44654088[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5[ppm]
Clipped           = TRUE
Mod_return        = 1
Scans             = 829.0
Total_scans       = 829.0

X_90_width        = 14.2[us]
X_acq_time        = 2.0840448[s]
X_angle           = 30[deg]
X_pulse           = 4.73333333[us]
Initial_wait      = 1[s]
Noe_time          = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 30
Relaxation_delay  = 2[s]
Temp_get          = 29[dC]
Unblank_time      = 2[us]
```

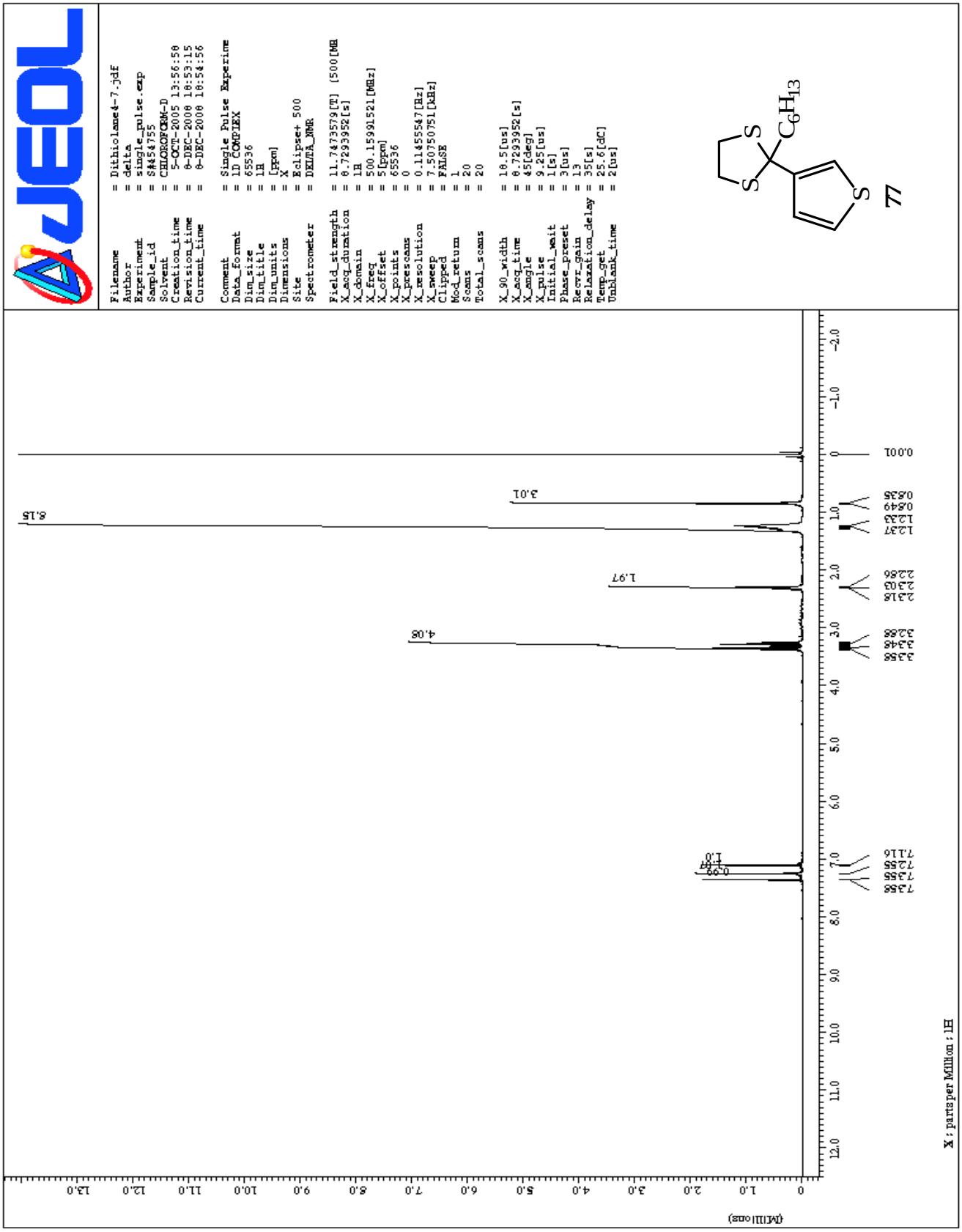


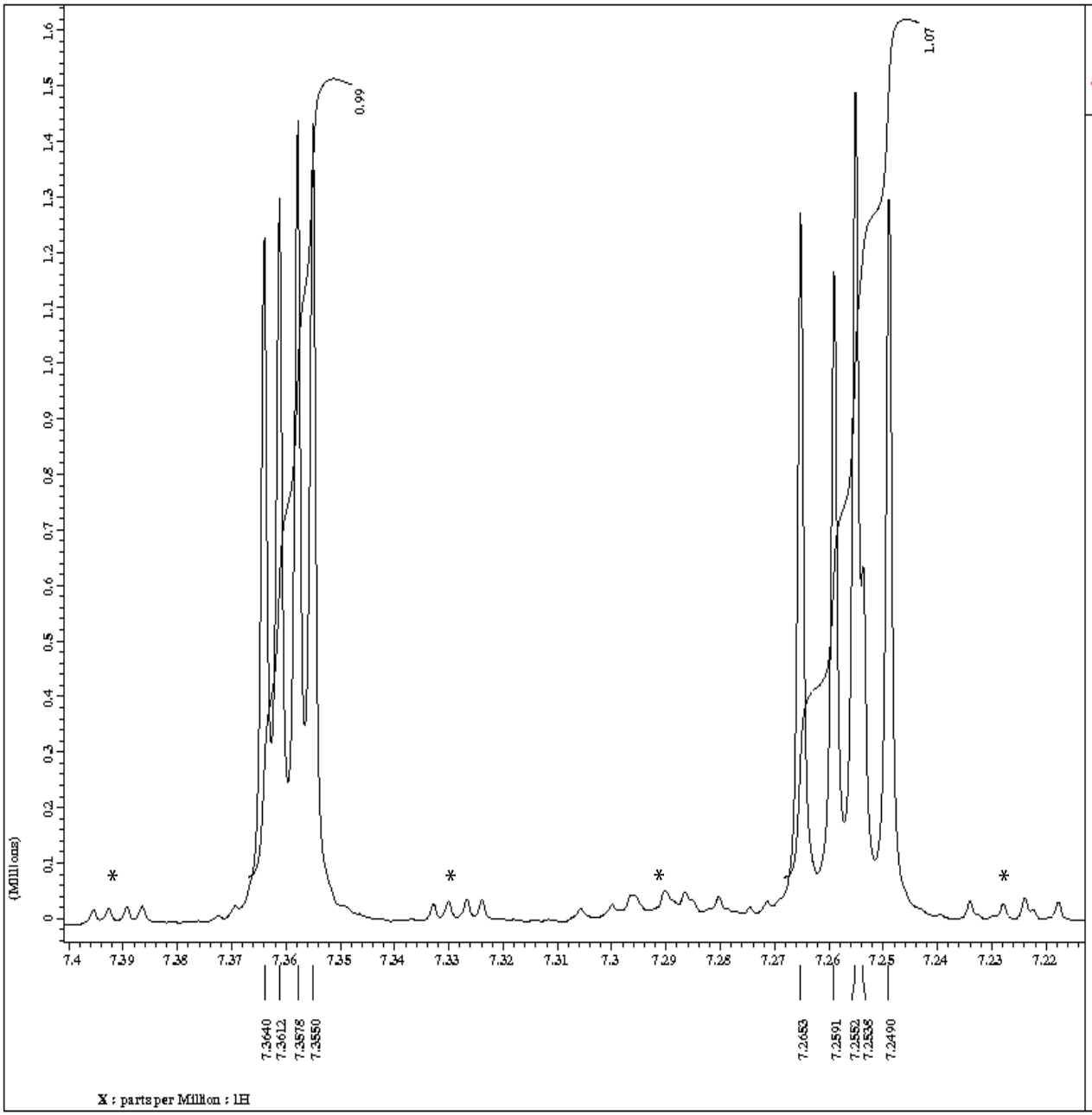
71


Digilab Win-IR Pro
hexyldithiane(2)
%Transmittance
Wavenumber
3102.2
2924.1
2854.6
1458.5
1423.1
1376.4
1362.4
1276.7
1212.5
1152.6
1112.6
1077.8
1007.4
862.1
727
636.1
796.9
778.6
664.5
614.7
C_6H_{13}
S
S
S
71

APPENDIX 3

^{1}H, ^{13}C NMR and IR spectra of 2-hexyl-2-thiophen-3-yl-1,3-dithiolane (**77**)


JEOL
Filename = Dithiolane4-7.jdf
Author = delta
Experiment = single_pulse.exp
Sample_id = S#454755
Solvent = CHLOROFORM-D
Creation_time = 5-OCT-2005 13:56:50
Revision_time = 6-DEC-2008 10:53:15
Current_time = 6-DEC-2008 10:54:56
Comment = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 65536
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 8.7293952[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 65536
X_prescans = 0
X_resolution = 0.11455547[Hz]
X_sweep = 7.50750751[kHz]
Clipped = FALSE
Mod_return = 1
Scans = 20
Total_scans = 20
X_90_width = 10.5[us]
X_acq_time = 8.7293952[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 13
Relaxation_delay = 35[s]
Temp_get = 25.6[dC]
Unblank_time = 2[us]
S
S
S
C_6H_{13}
77
8.15
3.01
1.97
4.08
1.00
0.99
0.001
0.835
0.849
1.233
1.237
2.316
2.303
2.286
3.358
3.348
3.288
7.358
7.355
7.255
7.116
(Million)
X : parts per Million : 1H

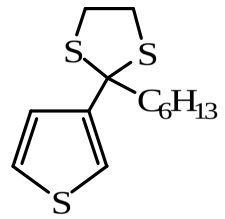


Filename = Dithiolane4-7.jdf
Author = delta
Experiment = single_pulse.exp
Sample_id = S#454755
Solvent = CHLOROFORM-D
Creation_time = 5-OCT-2005 13:56:58
Revision_time = 6-NOV-2008 13:41:12
Current_time = 6-NOV-2008 13:41:59

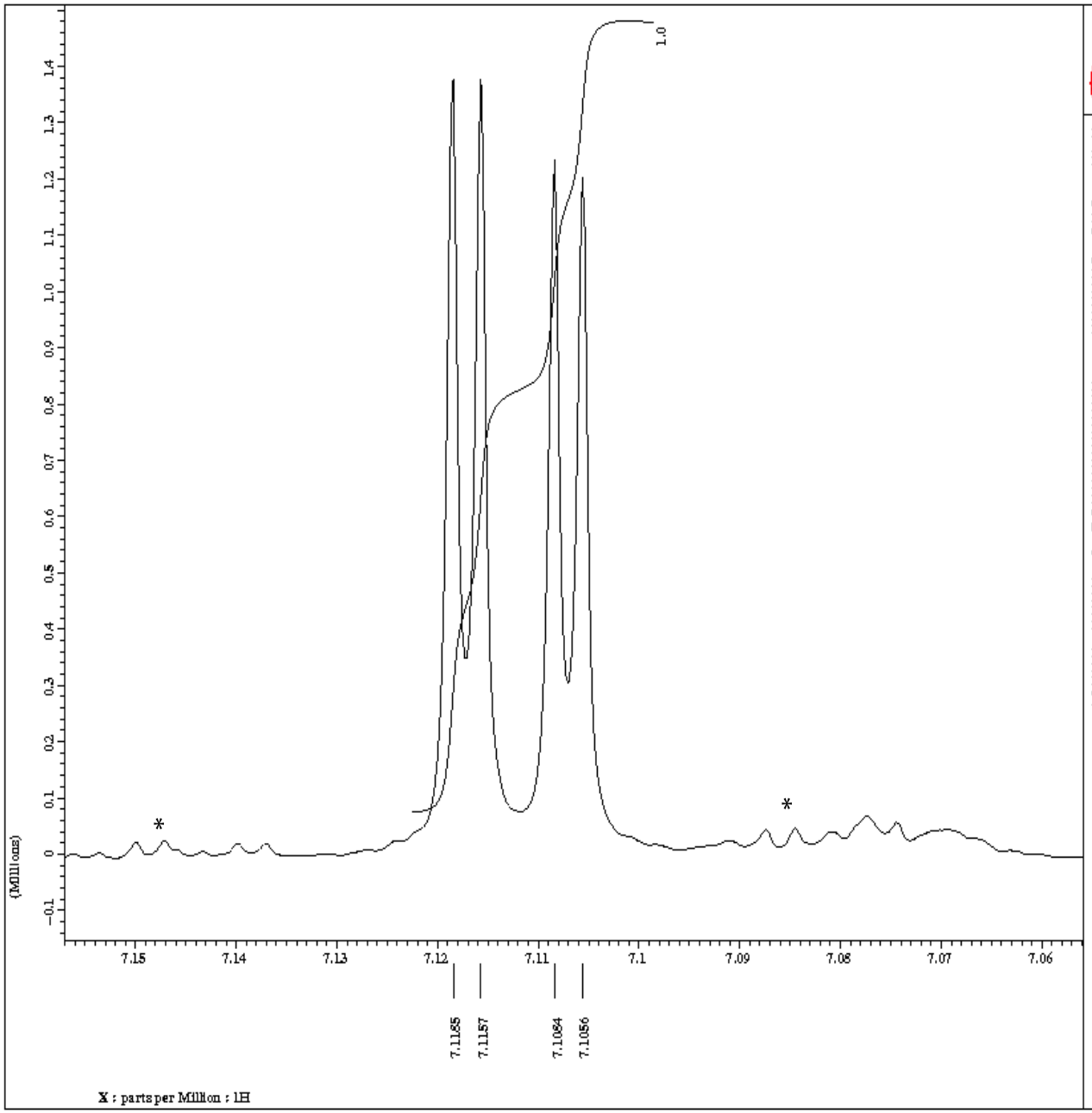
Comment = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 65536
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR

Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 0.7293952[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 65536
X_prescans = 0
X_resolution = 0.11455547[Hz]
X_sweep = 7.50750751[kHz]
Clipped = FALSE
Mod_return = 1
Scans = 20
Total_scans = 20

X_90_width = 10.5[us]
X_acq_time = 0.7293952[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 13
Relaxation_delay = 35[s]
Temp_get = 25.6[dC]
Unblank_time = 2[us]



77



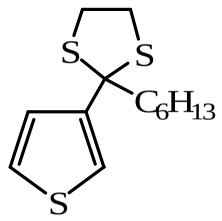
JEOL

```
Filename          = Dithiolane4-7.jdf
Author            = delta
Experiment        = single_pulse.exp
Sample_id         = S#454755
Solvent           = CHLOROFORM-D
Creation_time     =  5-OCT-2005 13:56:58
Revision_time     =  6-NOV-2008 13:41:12
Current_time      =  6-NOV-2008 13:44:36

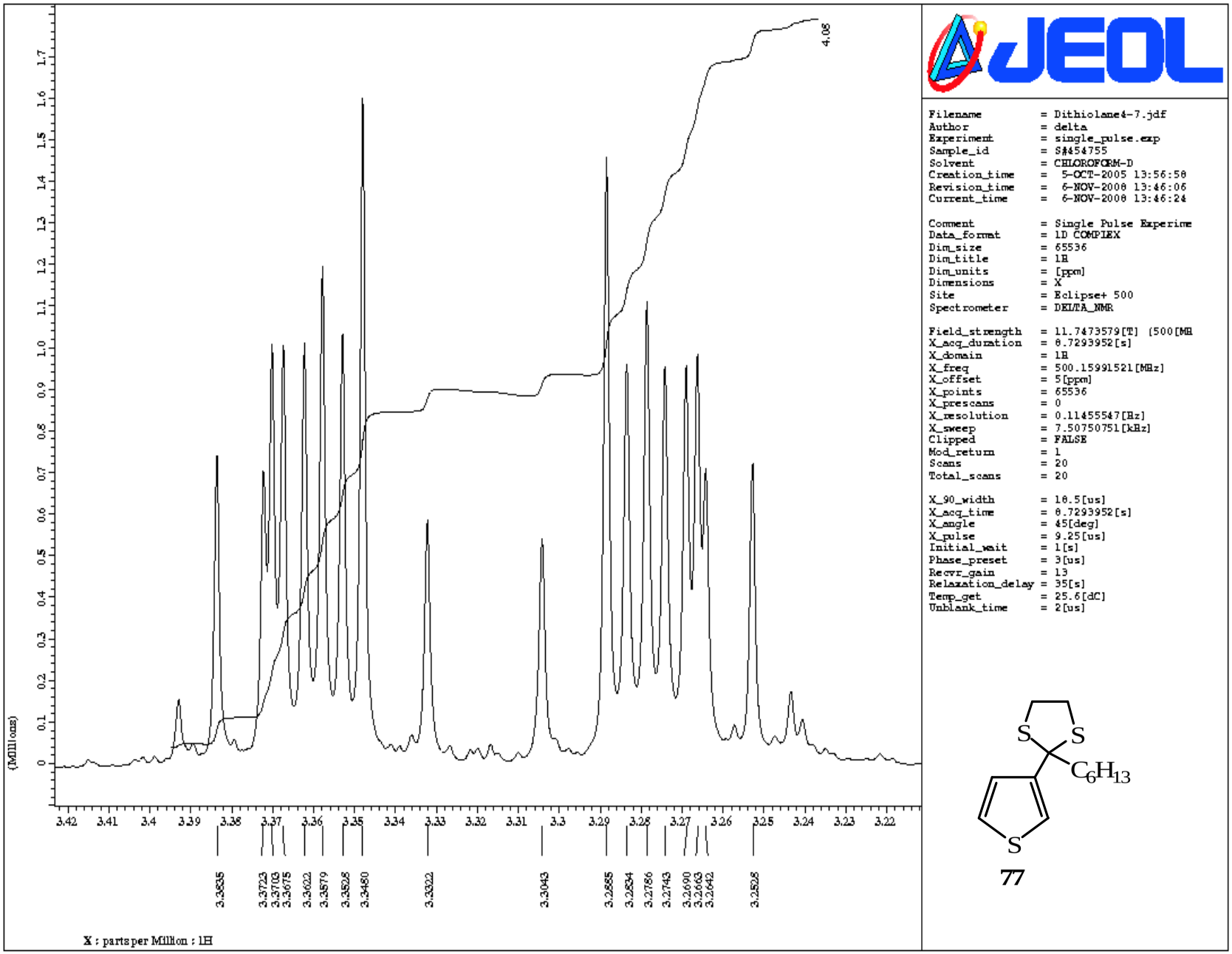
Comment           = Single Pulse Experime
Data_format       = 1D COMPLEX
Dim_size          = 65536
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

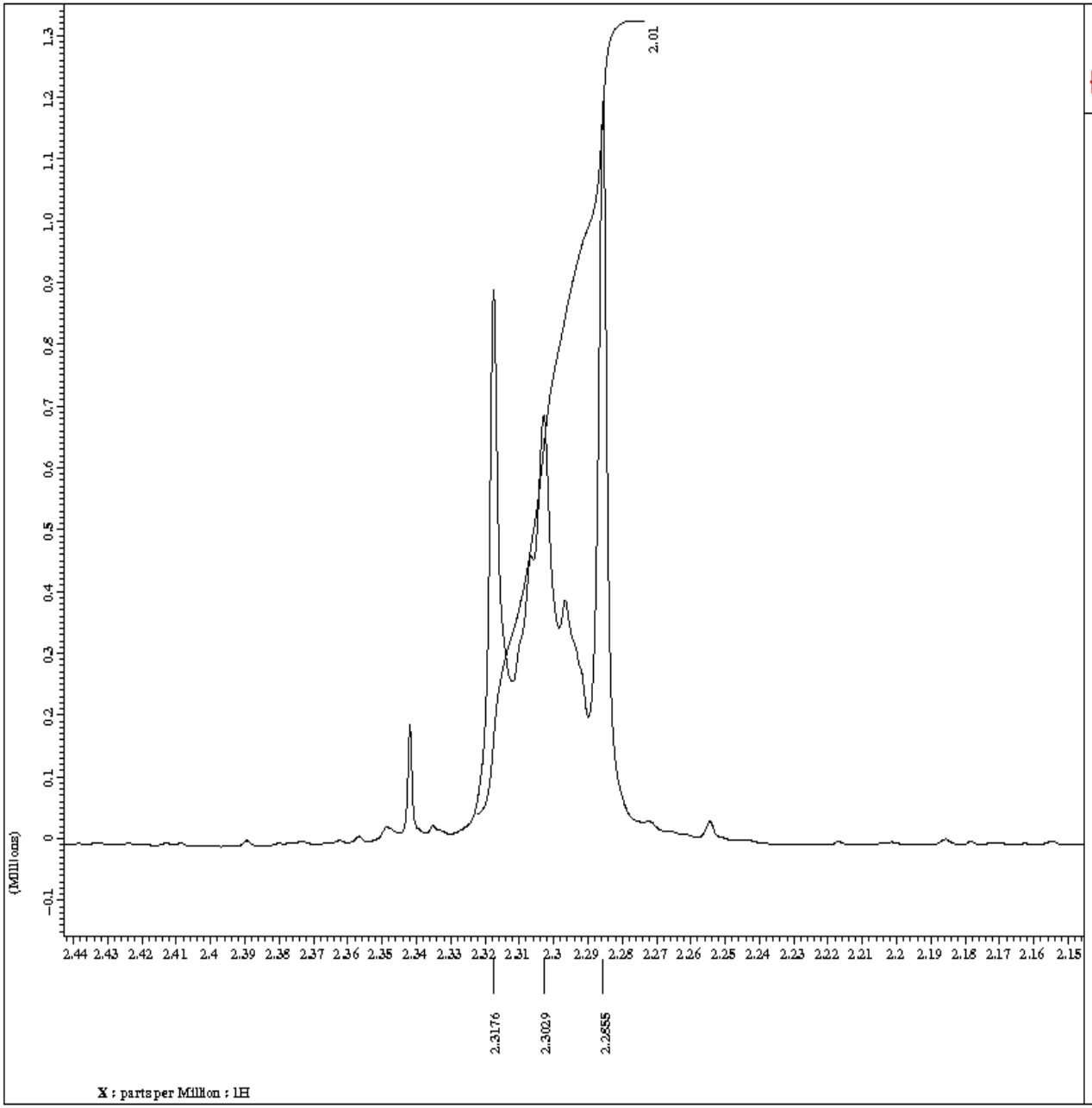
Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 0.7293952[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 5[ppm]
X_points          = 65536
X_prescans        = 0
X_resolution      = 0.11455547[Hz]
X_sweep           = 7.50750751[kHz]
Clipped           = FALSE
Mod_return        = 1
Scans             = 20
Total_scans       = 20

X_90_width        = 10.5[us]
X_acq_time        = 0.7293952[s]
X_angle           = 45[deg]
X_pulse           = 9.25[us]
Initial_wait      = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 13
Relaxation_delay  = 35[s]
Temp_get          = 25.6[dC]
Unblank_time      = 2[us]
```



77


4.08
(Millions)
3.42 3.41 3.4 3.39 3.38 3.37 3.36 3.35 3.34 3.33 3.32 3.31 3.3 3.29 3.28 3.27 3.26 3.25 3.24 3.23 3.22
3.3835
3.3723
3.3703
3.3675
3.3622
3.3579
3.3528
3.3480
3.3322
3.3043
3.2885
3.2824
3.2786
3.2743
3.2690
3.2663
3.2642
3.2508
X : parts per Million : 1H
Filename = Dithiolane4-7.jdf
Author = delta
Experiment = single_pulse.exp
Sample_id = S#454755
Solvent = CHLOROFORM-D
Creation_time = 5-OCT-2005 13:56:58
Revision_time = 6-NOV-2008 13:46:06
Current_time = 6-NOV-2008 13:46:24
Comment = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 65536
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 0.7293952[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 65536
X_prescans = 0
X_resolution = 0.11455547[Hz]
X_sweep = 7.50750751[kHz]
Clipped = FALSE
Mod_return = 1
Scans = 20
Total_scans = 20
X_90_width = 10.5[us]
X_acq_time = 0.7293952[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 13
Relaxation_delay = 35[s]
Temp_get = 25.6[dC]
Unblank_time = 2[us]
S
S
C6H13
S
77



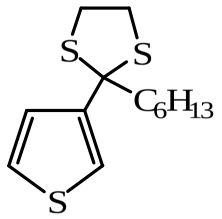
JEOL

```
Filename          = Dithiolane4-7.jdf
Author            = delta
Experiment        = single_pulse.exp
Sample_id         = S#454755
Solvent           = CHLOROFORM-D
Creation_time     =  5-OCT-2005 13:56:58
Revision_time     =  6-NOV-2008 13:46:06
Current_time      =  6-NOV-2008 13:49:33

Comment           = Single Pulse Experime
Data_format       = 1D COMPLEX
Dim_size          = 65536
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 0.7293952[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 5[ppm]
X_points          = 65536
X_prescans        = 0
X_resolution      = 0.11455547[Hz]
X_sweep           = 7.50750751[kHz]
Clipped           = FALSE
Mod_return        = 1
Scans             = 20
Total_scans       = 20

X_90_width        = 10.5[us]
X_acq_time        = 0.7293952[s]
X_angle           = 45[deg]
X_pulse           = 9.25[us]
Initial_wait      = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 13
Relaxation_delay  = 35[s]
Temp_get          = 25.6[dC]
Unblank_time      = 2[us]
```



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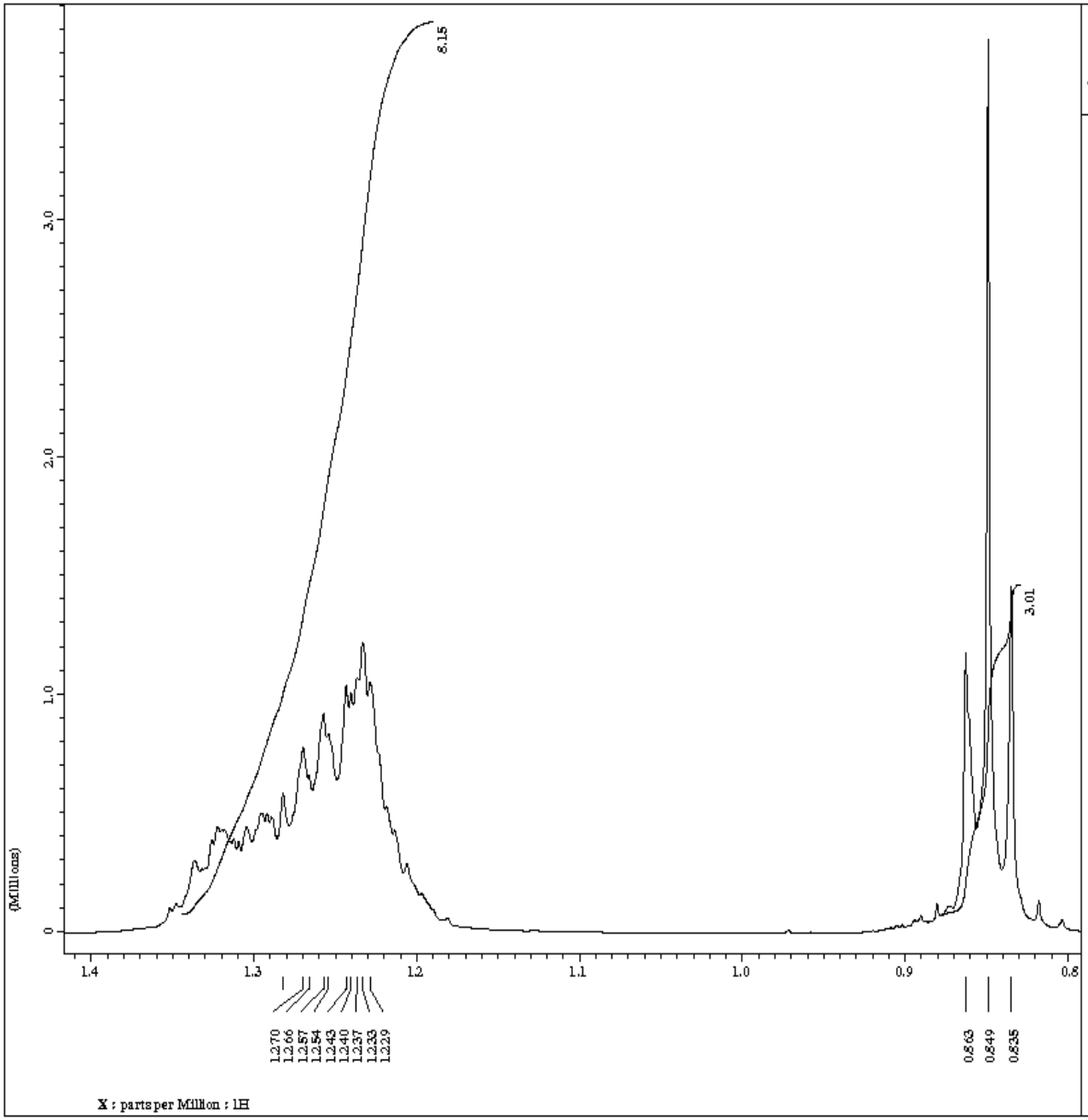


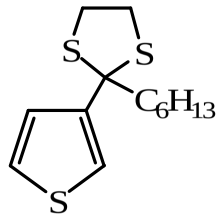
JEOL

```
Filename          = Dithiolane4-7.jdf
Author            = delta
Experiment        = single_pulse.exp
Sample_id         = S#454755
Solvent           = CHLOROFORM-D
Creation_time     =  5-OCT-2005 13:56:58
Revision_time     =  8-DEC-2008 18:53:15
Current_time      =  8-DEC-2008 19:06:19

Comment           = Single Pulse Experime
Data_format       = 1D COMPLEX
Dim_size          = 65536
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 0.7293952[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 5[ppm]
X_points          = 65536
X_prescans        = 0
X_resolution      = 0.11455547[Hz]
X_sweep           = 7.50750751[kHz]
Clipped           = FALSE
Mod_return        = 1
Scans             = 20
Total_scans       = 20

X_90_width        = 18.5[us]
X_acq_time        = 0.7293952[s]
X_angle           = 45[deg]
X_pulse           = 9.25[us]
Initial_wait      = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 13
Relaxation_delay  = 35[s]
Temp_get          = 25.6[dC]
Unblank_time      = 2[us]
```



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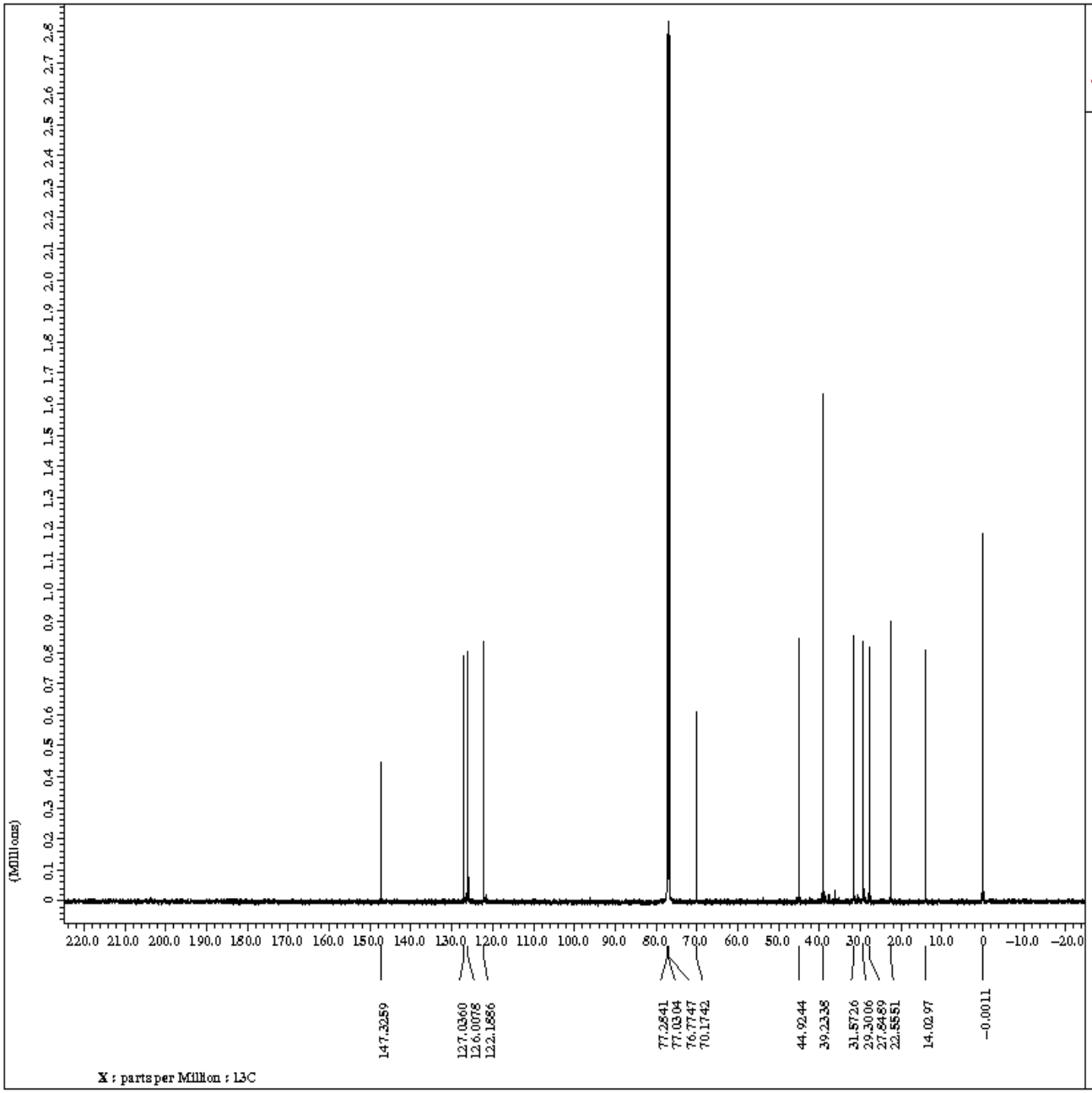
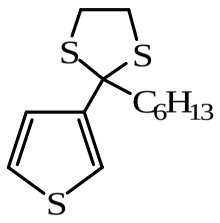
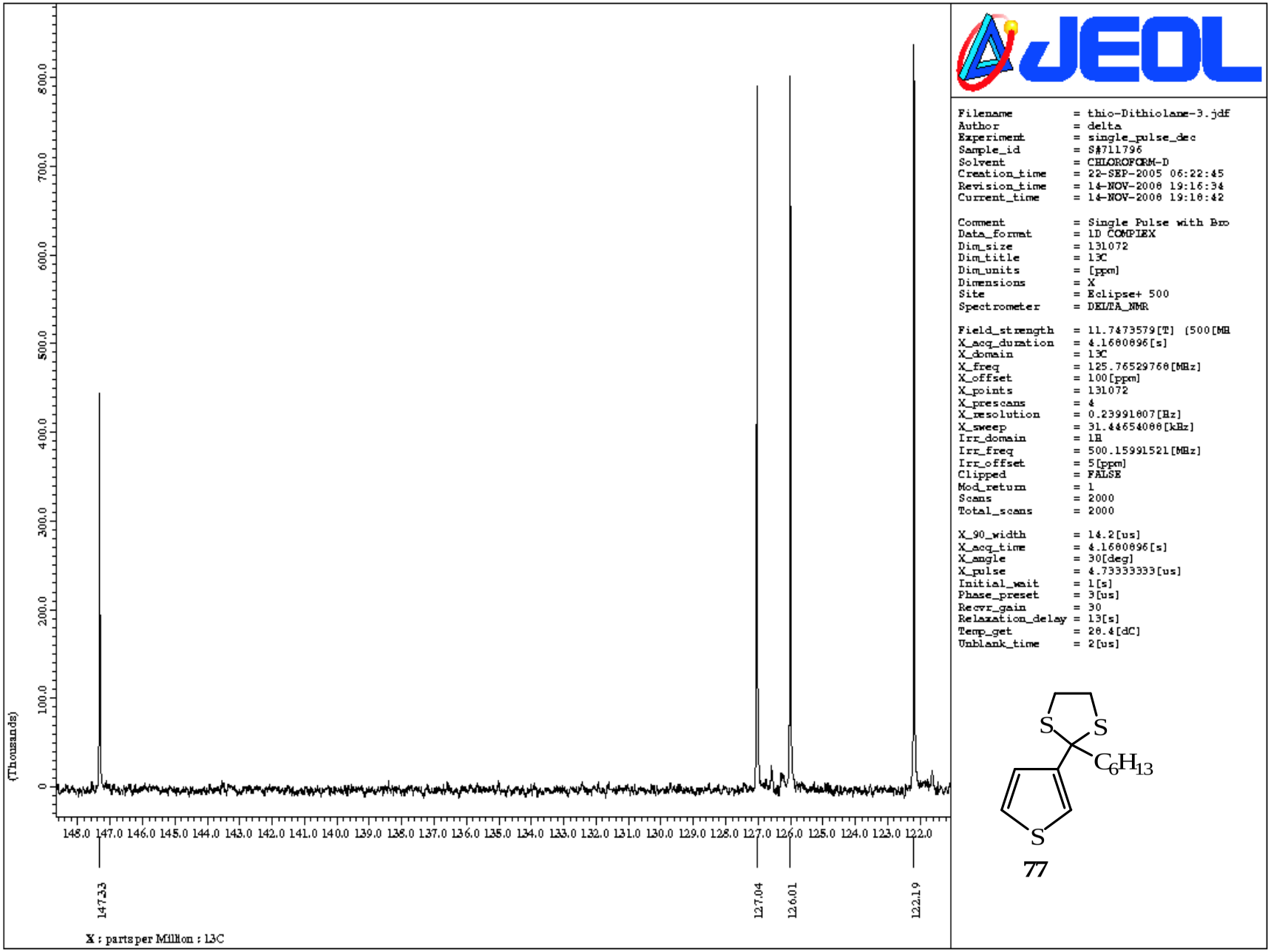


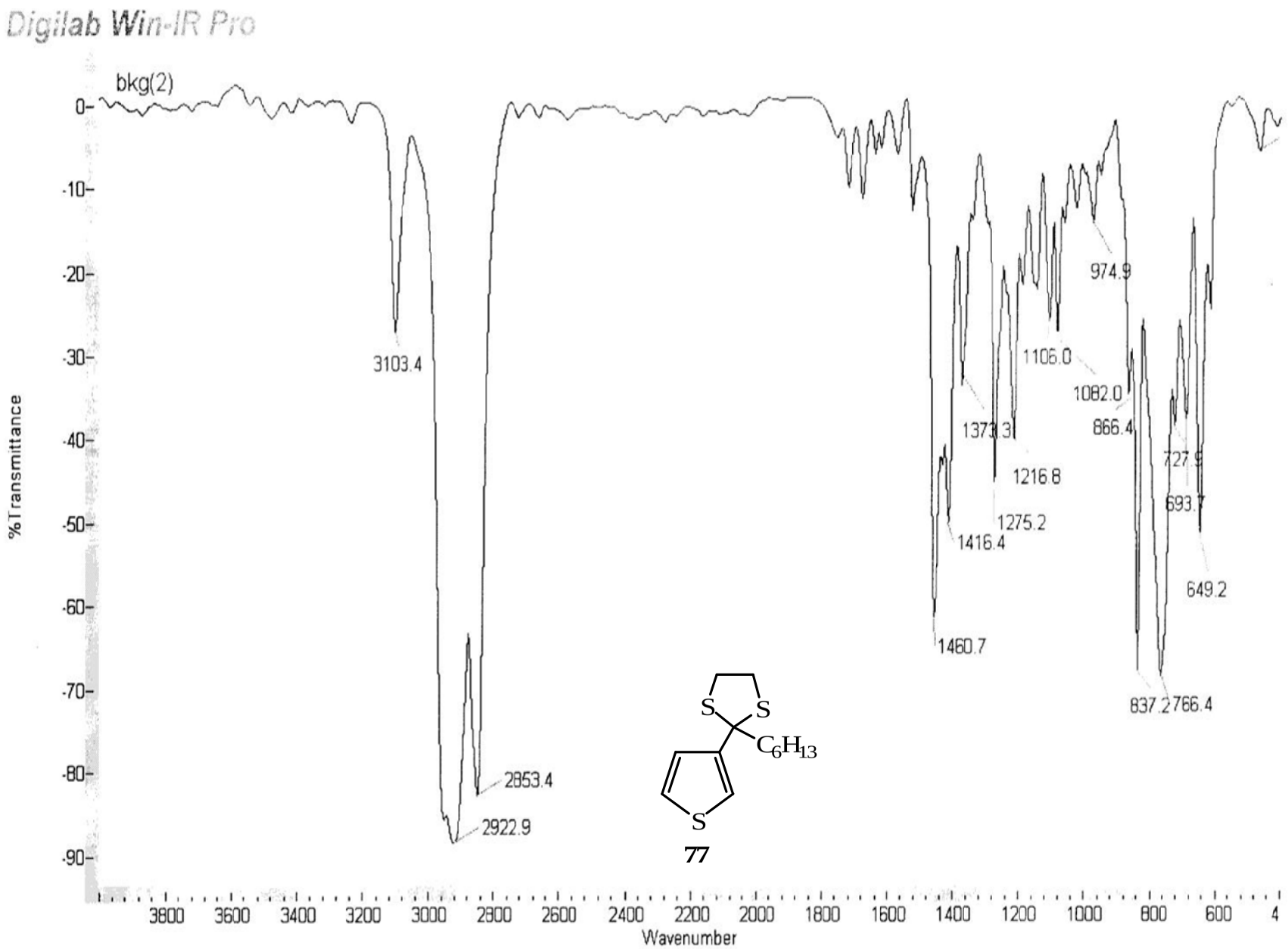
JEOL

Filename	= thio-Dithiolane-3.jdf
Author	= delta
Experiment	= single_pulse_dec
Sample_id	= S#711796
Solvent	= CHLOROFORM-D
Creation_time	= 22-SEP-2005 06:22:45
Revision_time	= 29-OCT-2008 18:53:00
Current_time	= 29-OCT-2008 18:53:59
Comment	= Single Pulse with Bro
Data_format	= 1D COMPLEX
Dim_size	= 131072
Dim_title	= 13C
Dim_units	= [ppm]
Dimensions	= X
Site	= Eclipse+ 500
Spectrometer	= DELTA_NMR
Field_strength	= 11.7473579[T] (500[MH
X_acq_duration	= 4.1680896[s]
X_domain	= 13C
X_freq	= 125.76529768[MHz]
X_offset	= 100[ppm]
X_points	= 131072
X_prescans	= 4
X_resolution	= 0.23991807[Hz]
X_sweep	= 31.44654088[kHz]
Irr_domain	= 1H
Irr_freq	= 500.15991521[MHz]
Irr_offset	= 5[ppm]
Clipped	= FALSE
Mod_return	= 1
Scans	= 2000
Total_scans	= 2000
X_90_width	= 14.2[us]
X_acq_time	= 4.1680896[s]
X_angle	= 30[deg]
X_pulse	= 4.73333333[us]
Initial_wait	= 1[s]
Phase_preset	= 3[us]
Recvr_gain	= 30
Relaxation_delay	= 13[s]
Temp_get	= 20.4[dC]
Unblank_time	= 2[us]



77

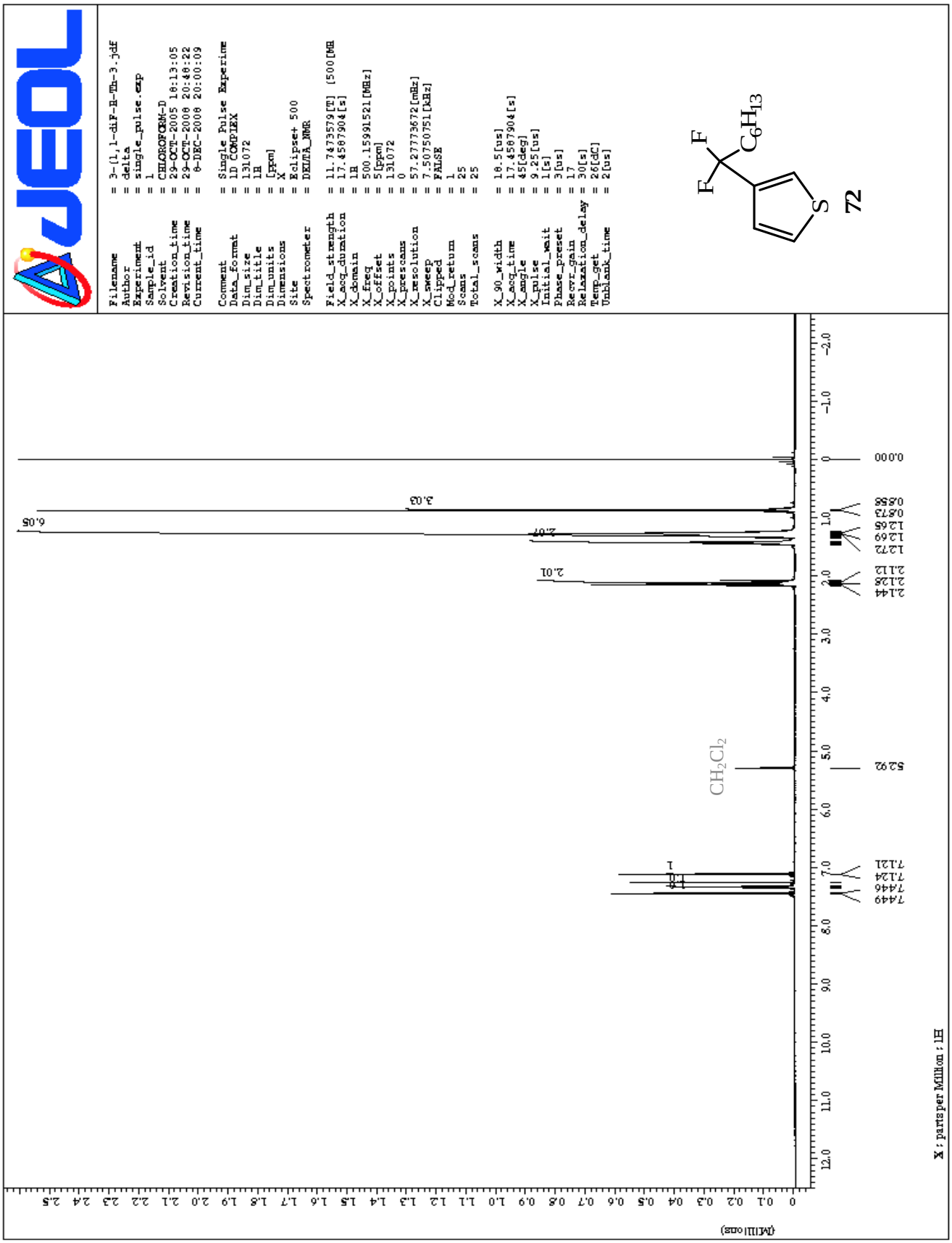

(Thousands)
800.0
700.0
600.0
500.0
400.0
300.0
200.0
100.0
0
148.0 147.0 146.0 145.0 144.0 143.0 142.0 141.0 140.0 139.0 138.0 137.0 136.0 135.0 134.0 133.0 132.0 131.0 130.0 129.0 128.0 127.0 126.0 125.0 124.0 123.0 122.0
147.33
127.04
126.01
122.19
X : parts per Million : 13C
JEOL
Filename = thio-Dithiolane-3.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = S#711796
Solvent = CHLOROFORM-D
Creation_time = 22-SEP-2005 06:22:45
Revision_time = 14-NOV-2008 19:16:34
Current_time = 14-NOV-2008 19:16:42
Comment = Single Pulse with Dec
Data_format = 1D COMPLEX
Dim_size = 131072
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 4.1680896[s]
X_domain = 13C
X_freq = 125.76529760[MHz]
X_offset = 100[ppm]
X_points = 131072
X_prescans = 4
X_resolution = 0.23991807[Hz]
X_sweep = 31.44654008[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 2000
Total_scans = 2000
X_90_width = 14.2[us]
X_acq_time = 4.1680896[s]
X_angle = 30[deg]
X_pulse = 4.73333333[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 30
Relaxation_delay = 13[s]
Temp_get = 28.4[dC]
Unblank_time = 2[us]
S
S
C6H13
S
77

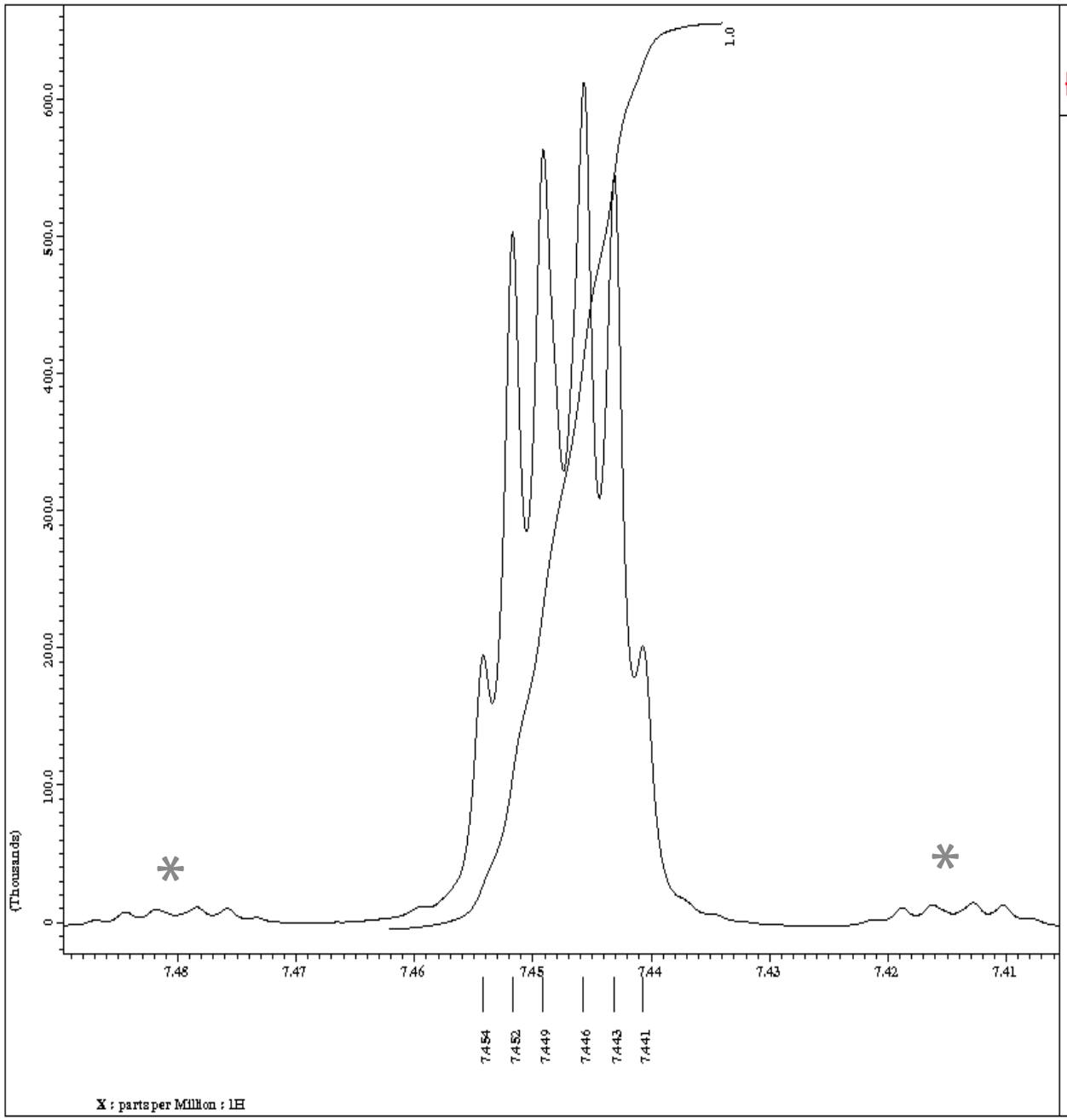

Digilab Win-IR Pro
bkg(2)
%Transmittance
Wavenumber
3103.4
2922.9
2853.4
1460.7
1416.4
1373.3
1275.2
1216.8
1106.0
1082.0
974.9
866.4
837.2
766.4
727.9
693.7
649.2
S
S
S
C6H13

77

APPENDIX 4

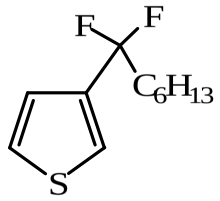
^{1}H, ^{13}C and ^{19}F NMR spectra of 3-(1,1-difluoroheptyl)thiophene (**72**)


JEOL
Filename = 3-(1,1-diF-B-Th-3.jdf
Author = delta
Experiment = single_pulse.exp
Sample_id = 1
Solvent = CHLOROFORM-D
Creation_time = 29-OCT-2005 18:13:05
Revision_time = 29-OCT-2008 20:48:22
Current_time = 6-DEC-2008 20:00:09
Comment = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 131072
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] [500[MH
X_acq_duration = 17.4587904[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 131072
X_prescans = 0
X_resolution = 57.27773672[mHz]
X_sweep = 7.507507751[kHz]
Clipped = FALSE
Mod_return = 1
Scans = 25
Total_scans = 25
X_90_width = 18.5[us]
X_acq_time = 17.4587904[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 17
Relaxation_delay = 30[s]
Temp_get = 26[dC]
Unblank_time = 2[us]
F
F
C_6H_{13}
S
72
6.05
3.03
2.07
2.01
CH_2Cl_2
1
0.000
0.858
0.873
1.265
1.269
1.272
2.112
2.128
2.144
5.292
7.121
7.124
7.446
7.449
X : parts per Million : 1H

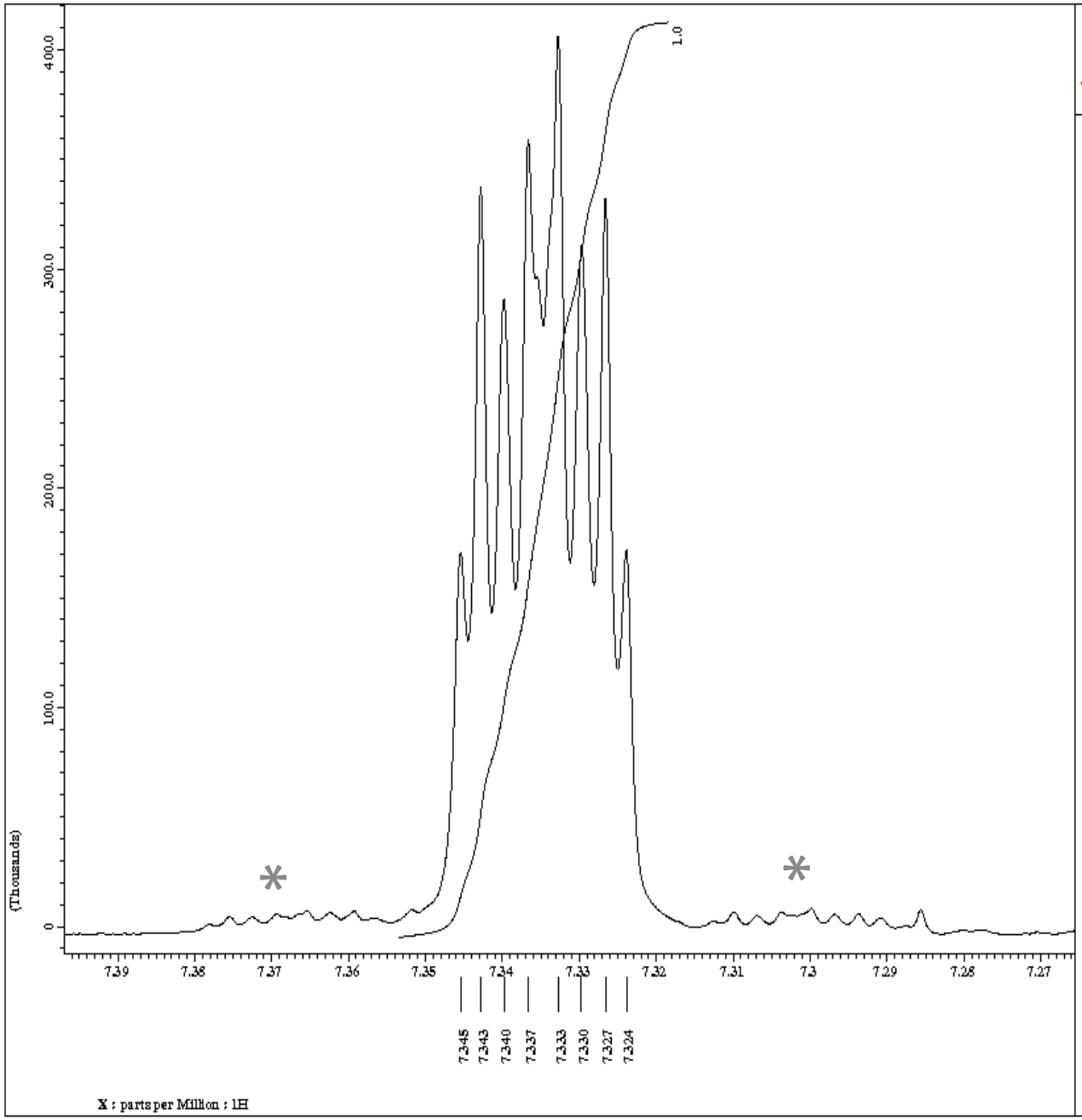


JEOL

Filename	= 3-(1,1-diF-H-Th-3.jdf
Author	= delta
Experiment	= single_pulse.exp
Sample_id	= 1
Solvent	= CHLOROFORM-D
Creation_time	= 29-OCT-2005 10:13:05
Revision_time	= 29-OCT-2008 20:48:22
Current_time	= 6-DEC-2008 20:08:43
Comment	= Single Pulse Experime
Data_format	= 1D COMPLEX
Dim_size	= 131072
Dim_title	= 1H
Dim_units	= [ppm]
Dimensions	= X
Site	= Eclipse+ 500
Spectrometer	= DELTA_NMR
Field_strength	= 11.7473579[T] (500[MH
X_acq_duration	= 17.4587904[s]
X_domain	= 1H
X_freq	= 500.15991521[MHz]
X_offset	= 5[ppm]
X_points	= 131072
X_prescans	= 0
X_resolution	= 57.27773672[mHz]
X_sweep	= 7.50750751[kHz]
Clipped	= FALSE
Mod_return	= 1
Scans	= 25
Total_scans	= 25
X_90_width	= 10.5[us]
X_acq_time	= 17.4587904[s]
X_angle	= 45[deg]
X_pulse	= 9.25[us]
Initial_wait	= 1[s]
Phase_preset	= 3[us]
Recvr_gain	= 17
Relaxation_delay	= 30[s]
Temp_get	= 26[dC]
Unblank_time	= 2[us]



72



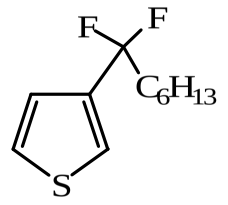
JEOL

```
Filename          = 3-(1,1-diF-H-Th-3.jdf
Author            = delta
Experiment        = single_pulse.exp
Sample_id         = 1
Solvent           = CHLOROFORM-D
Creation_time     = 29-OCT-2005 18:13:05
Revision_time     = 29-OCT-2008 20:48:22
Current_time      =  8-DEC-2008 20:11:58

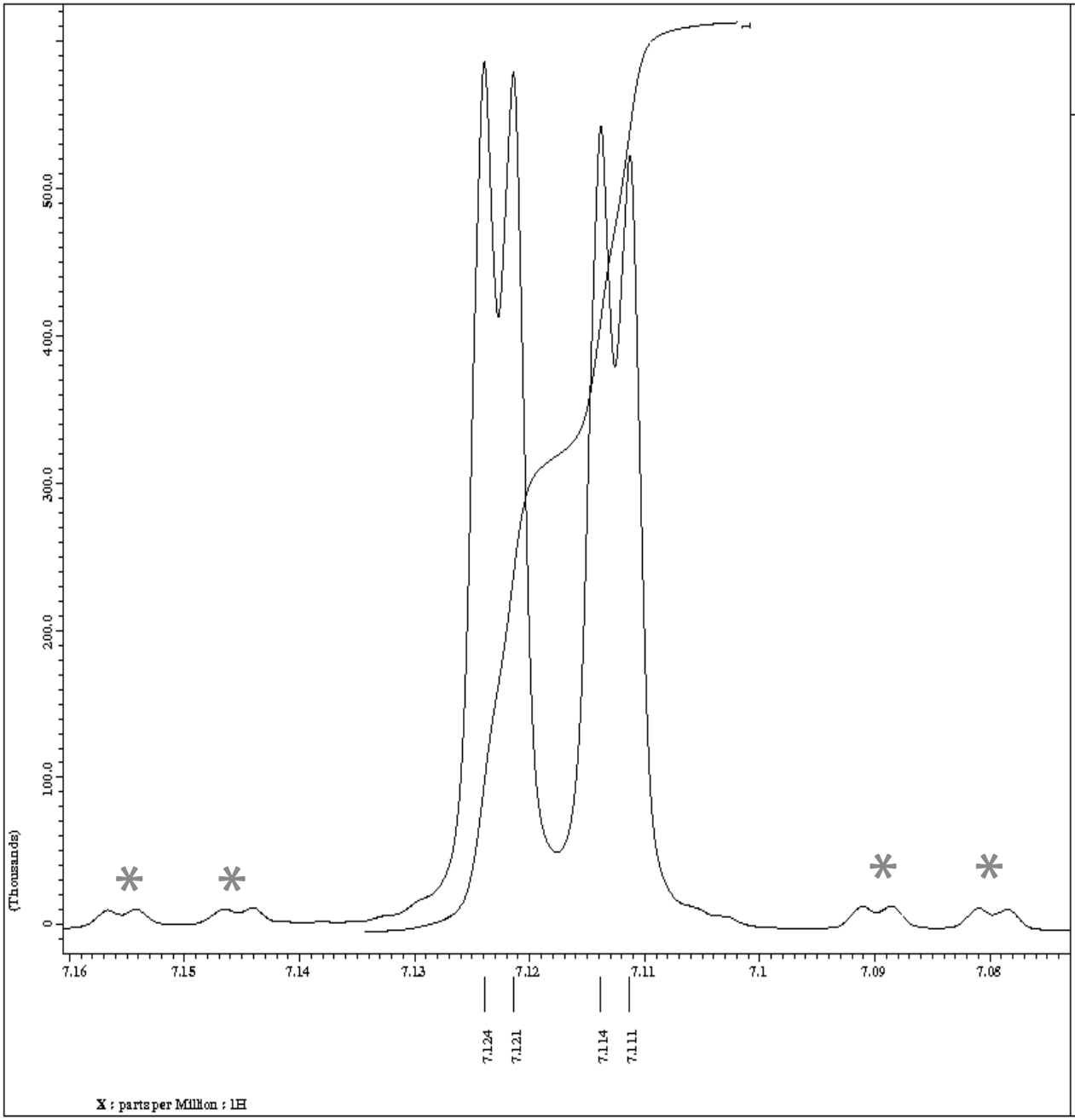
Comment           = Single Pulse Experime
Data_format       = 1D COMPLEX
Dim_size          = 131072
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 17.4587904[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 5[ppm]
X_points          = 131072
X_prescans        = 0
X_resolution      = 57.27773672[mHz]
X_sweep           = 7.50750751[kHz]
Clipped           = FALSE
Mod_return        = 1
Scans             = 25
Total_scans       = 25

X_90_width        = 18.5[us]
X_acq_time        = 17.4587904[s]
X_angle           = 45[deg]
X_pulse           = 9.25[us]
Initial_wait      = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 17
Relaxation_delay  = 30[s]
Temp_get          = 26[dC]
Unblank_time      = 2[us]
```



72

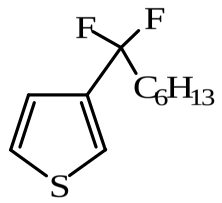



```
Filename          = 3-(1,1-diF-H-Th-3.jdf
Author            = delta
Experiment        = single_pulse.exp
Sample_id         = 1
Solvent           = CHLOROFORM-D
Creation_time     = 29-OCT-2005 18:13:05
Revision_time     = 29-OCT-2008 20:48:22
Current_time      =  8-DEC-2008 20:15:05

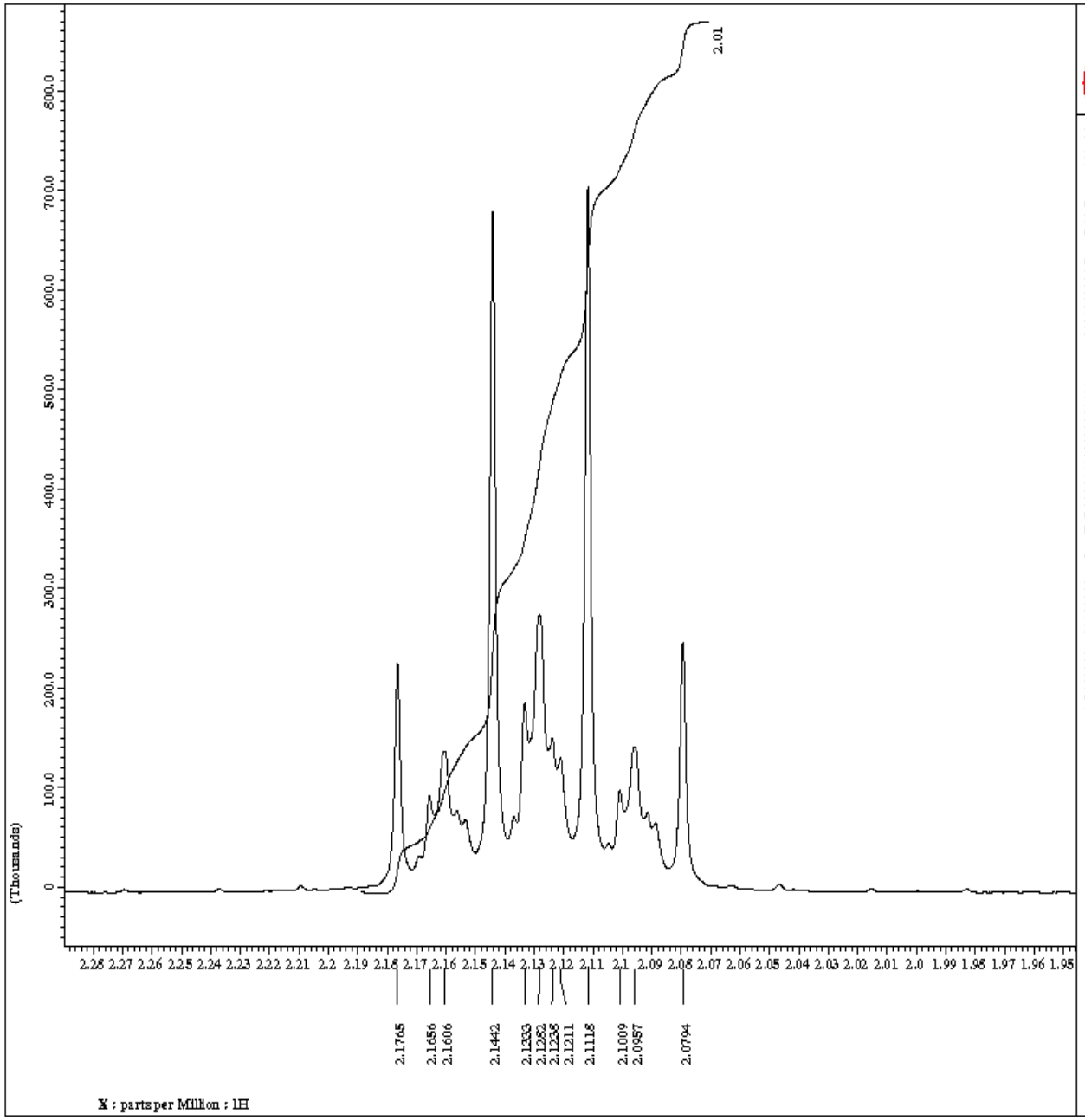
Comment           = Single Pulse Experime
Data_format       = 1D COMPLEX
Dim_size          = 131072
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 17.4587904[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 5[ppm]
X_points          = 131072
X_prescans        = 0
X_resolution      = 57.27773672[mHz]
X_sweep           = 7.50750751[kHz]
Clipped           = FALSE
Mod_return        = 1
Scans             = 25
Total_scans       = 25

X_90_width        = 18.5[us]
X_acq_time        = 17.4587904[s]
X_angle           = 45[deg]
X_pulse           = 9.25[us]
Initial_wait      = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 17
Relaxation_delay  = 30[s]
Temp_get          = 26[dC]
Unblank_time      = 2[us]
```

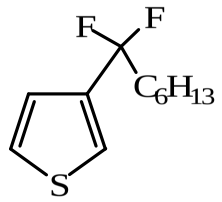


72

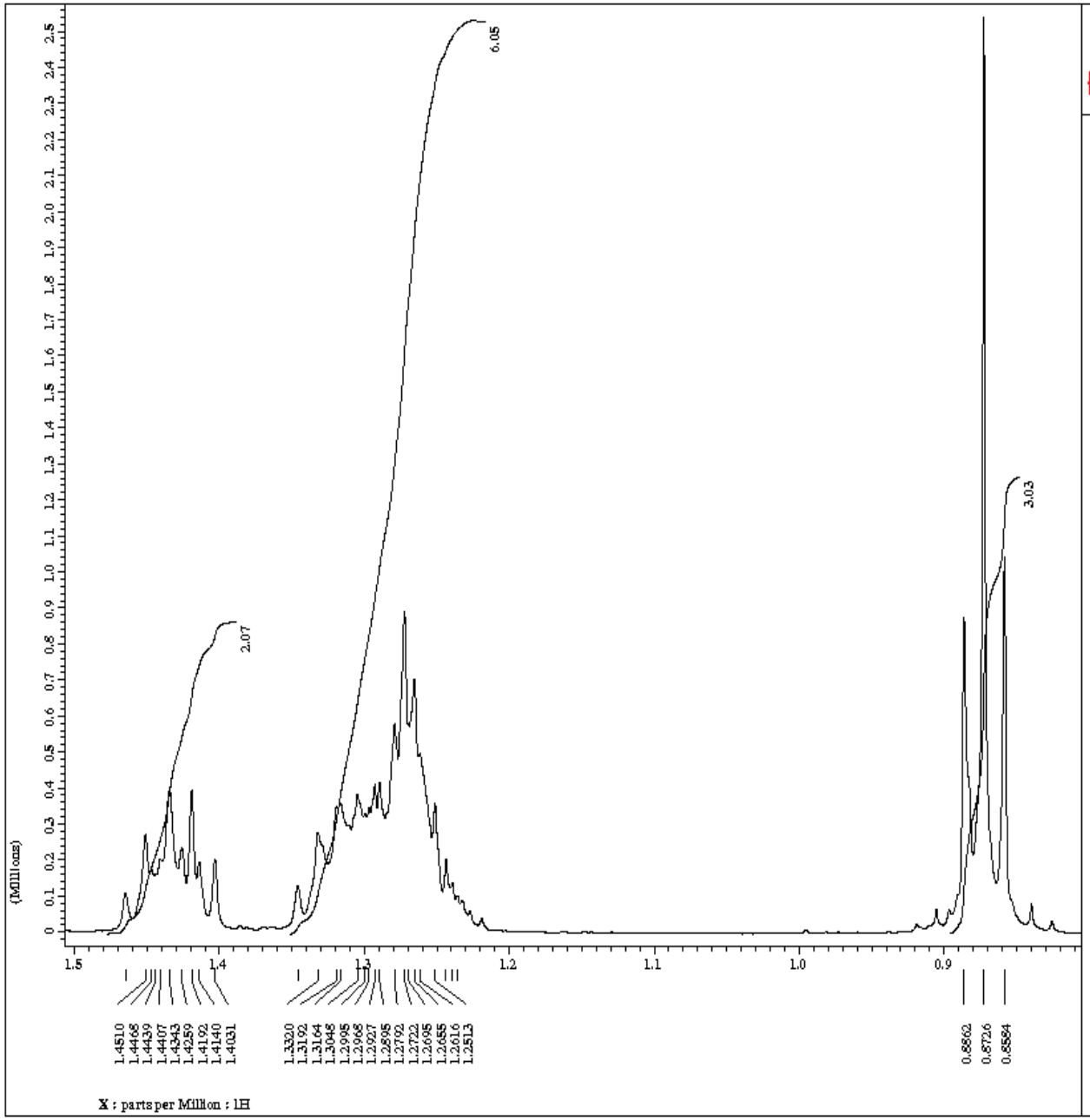


JEOL

Filename	= 3-(1,1-diF-H-Th-3.jdf
Author	= delta
Experiment	= single_pulse.exp
Sample_id	= 1
Solvent	= CHLOROFORM-D
Creation_time	= 29-OCT-2005 18:13:05
Revision_time	= 29-OCT-2008 20:04:10
Current_time	= 29-OCT-2008 20:04:30
Comment	= Single Pulse Experime
Data_format	= 1D COMPLEX
Dim_size	= 131072
Dim_title	= 1H
Dim_units	= [ppm]
Dimensions	= X
Site	= Eclipse+ 500
Spectrometer	= DELTA_NMR
Field_strength	= 11.7473579[T] (500[MH
X_acq_duration	= 17.458790&[s]
X_domain	= 1H
X_freq	= 500.15991521[MHz]
X_offset	= 5[ppm]
X_points	= 131072
X_prescans	= 0
X_resolution	= 57.27773672[mHz]
X_sweep	= 7.50750751[kHz]
Clipped	= FALSE
Mod_return	= 1
Scans	= 25
Total_scans	= 25
X_90_width	= 18.5[us]
X_acq_time	= 17.458790&[s]
X_angle	= 45[deg]
X_pulse	= 9.25[us]
Initial_wait	= 1[s]
Phase_preset	= 3[us]
Recvr_gain	= 17
Relaxation_delay	= 30[s]
Temp_get	= 26[dC]
Unblank_time	= 2[us]



72

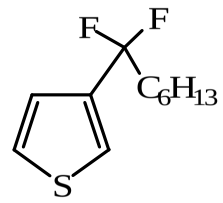


Filename = 3-(1,1-diF-H-Th-3.jdf
Author = delta
Experiment = single_pulse.exp
Sample_id = 1
Solvent = CHLOROFORM-D
Creation_time = 29-OCT-2005 10:13:05
Revision_time = 29-OCT-2008 20:48:22
Current_time = 29-OCT-2008 20:53:47

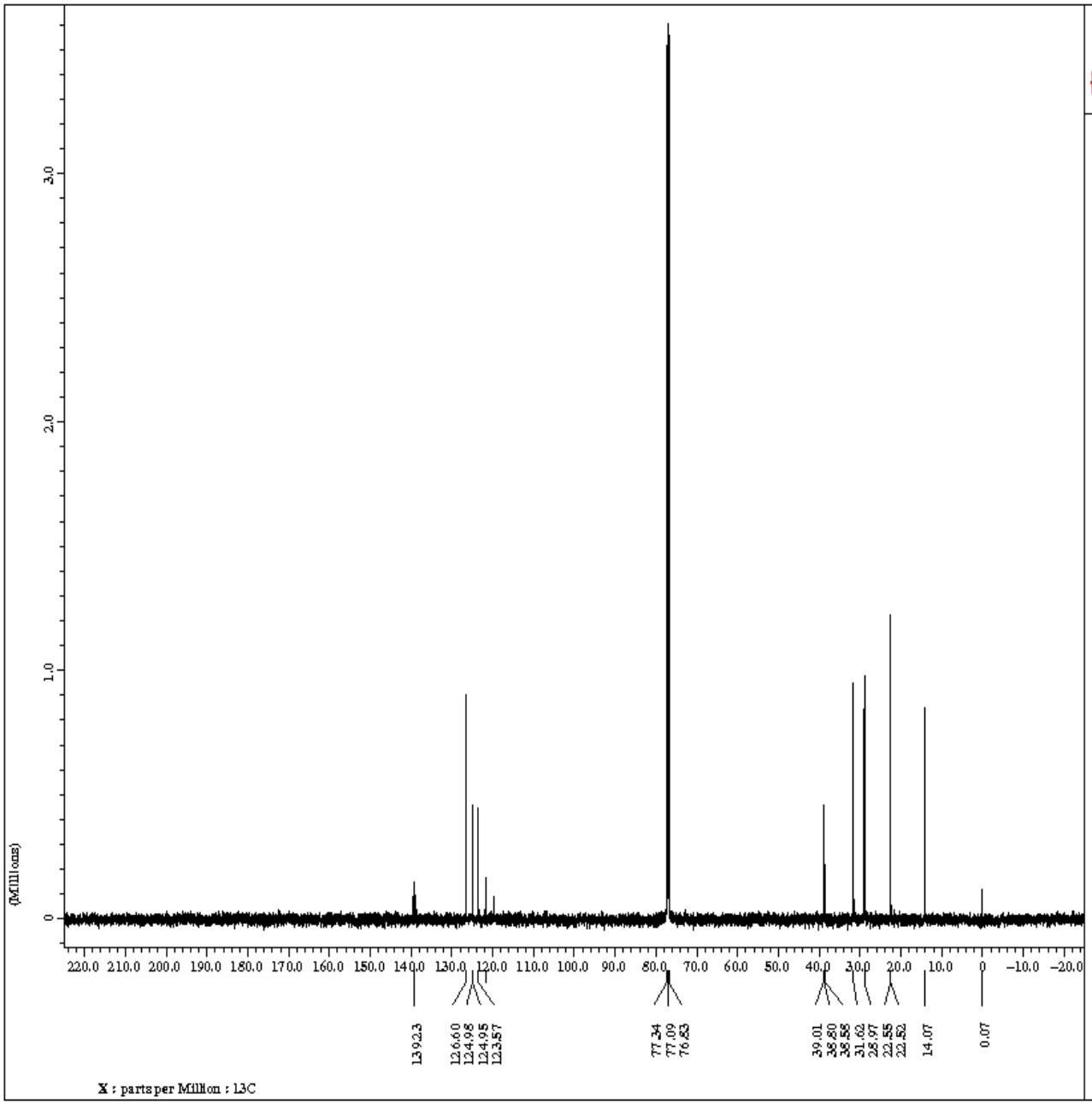
Comment = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 131072
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR

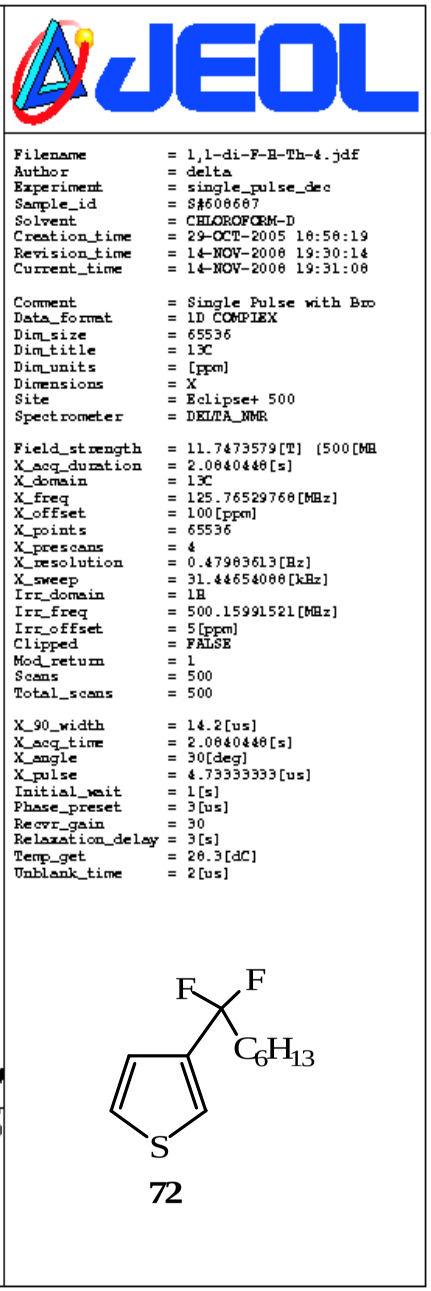
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 17.4587904[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 131072
X_prescans = 0
X_resolution = 57.27773672[mHz]
X_sweep = 7.50750751[kHz]
Clipped = FALSE
Mod_return = 1
Scans = 25
Total_scans = 25

X_90_width = 10.5[us]
X_acq_time = 17.4587904[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 17
Relaxation_delay = 30[s]
Temp_get = 26[dC]
Unblank_time = 2[us]



72





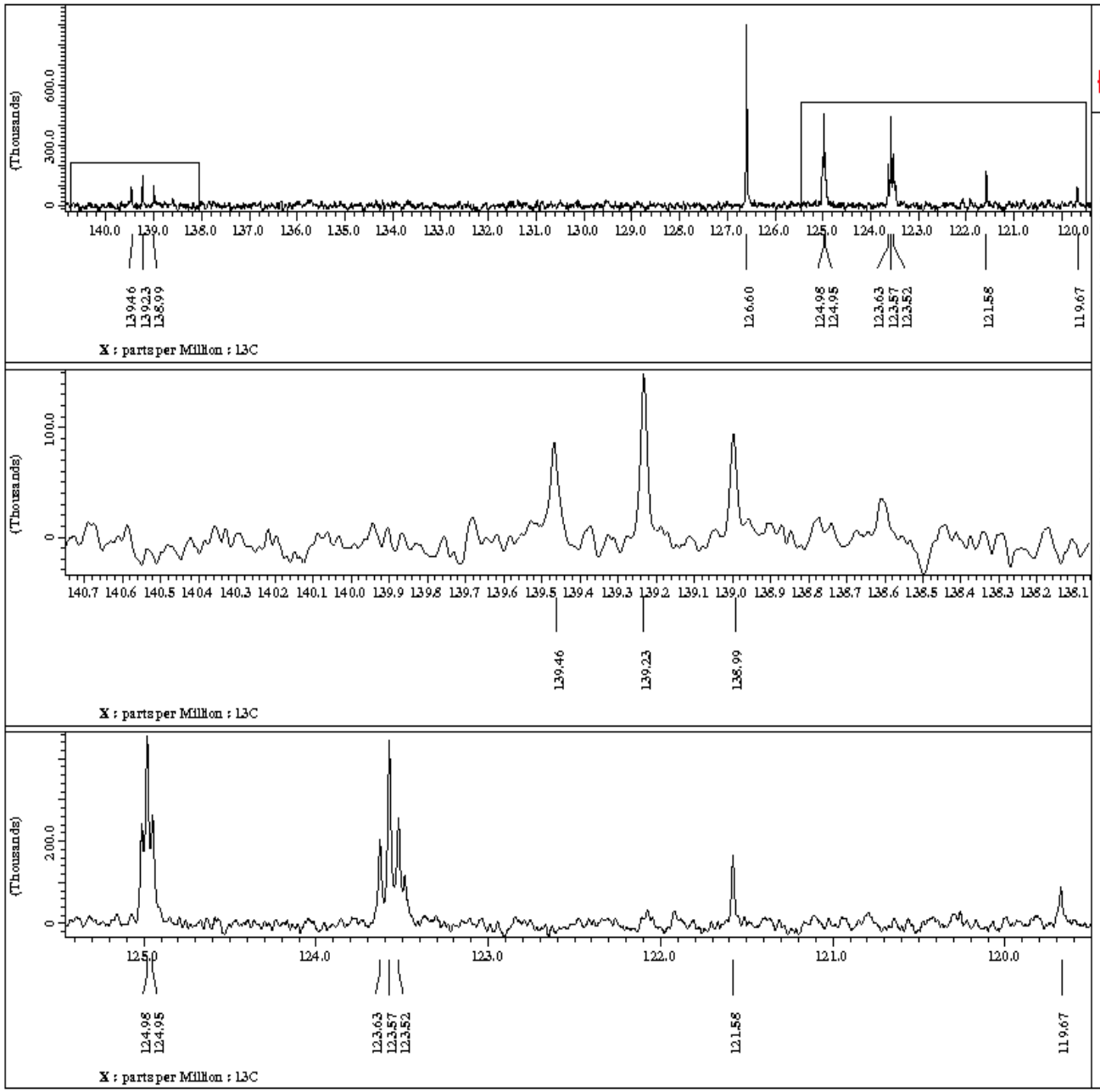

```
Filename          = 1,1-di-F-H-Th-4.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#600607
Solvent           = CHLOROFORM-D
Creation_time     = 29-OCT-2005 10:50:19
Revision_time     = 14-NOV-2008 19:30:14
Current_time      = 14-NOV-2008 19:31:08

Comment           = Single Pulse with Bro
Data_format       = 1D COMPLEX
Dim_size          = 65536
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 2.0840448[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 65536
X_prescans        = 4
X_resolution      = 0.47983613[Hz]
X_sweep           = 31.44654088[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 500
Total_scans       = 500

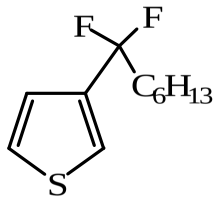
X_90_width        = 14.2[us]
X_acq_time        = 2.0840448[s]
X_angle           = 30[deg]
X_pulse           = 4.73333333[us]
Initial_wait      = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 30
Relaxation_delay  = 3[s]
Temp_get          = 26.3[dC]
Unblank_time      = 2[us]
```


72



JEOL

Filename	= 1,1-di-F-H-Th-4.jdf
Author	= delta
Experiment	= single_pulse_dec
Sample_id	= S#606687
Solvent	= CHLOROFORM-D
Creation_time	= 29-OCT-2005 10:50:19
Revision_time	= 14-NOV-2006 19:54:59
Current_time	= 14-NOV-2006 19:55:09
Comment	= Single Pulse with Bro
Data_format	= 1D COMPLEX
Dim_size	= 65536
Dim_title	= 13C
Dim_units	= [ppm]
Dimensions	= X
Site	= Eclipse+ 500
Spectrometer	= DELTA_NMR
Field_strength	= 11.7473579[T] (500[MH
X_acq_duration	= 2.0840448[s]
X_domain	= 13C
X_freq	= 125.76529760[MHz]
X_offset	= 100[ppm]
X_points	= 65536
X_prescans	= 4
X_resolution	= 0.47983613[Hz]
X_sweep	= 31.44654000[kHz]
Irr_domain	= 1H
Irr_freq	= 500.15991521[MHz]
Irr_offset	= 5[ppm]
Clipped	= FALSE
Mod_return	= 1
Scans	= 500
Total_scans	= 500
X_90_width	= 14.2[us]
X_acq_time	= 2.0840448[s]
X_angle	= 30[deg]
X_pulse	= 4.73333333[us]
Initial_wait	= 1[s]
Phase_preset	= 3[us]
Recvr_gain	= 30
Relaxation_delay	= 3[s]
Temp_get	= 20.3[dC]
Unblank_time	= 2[us]



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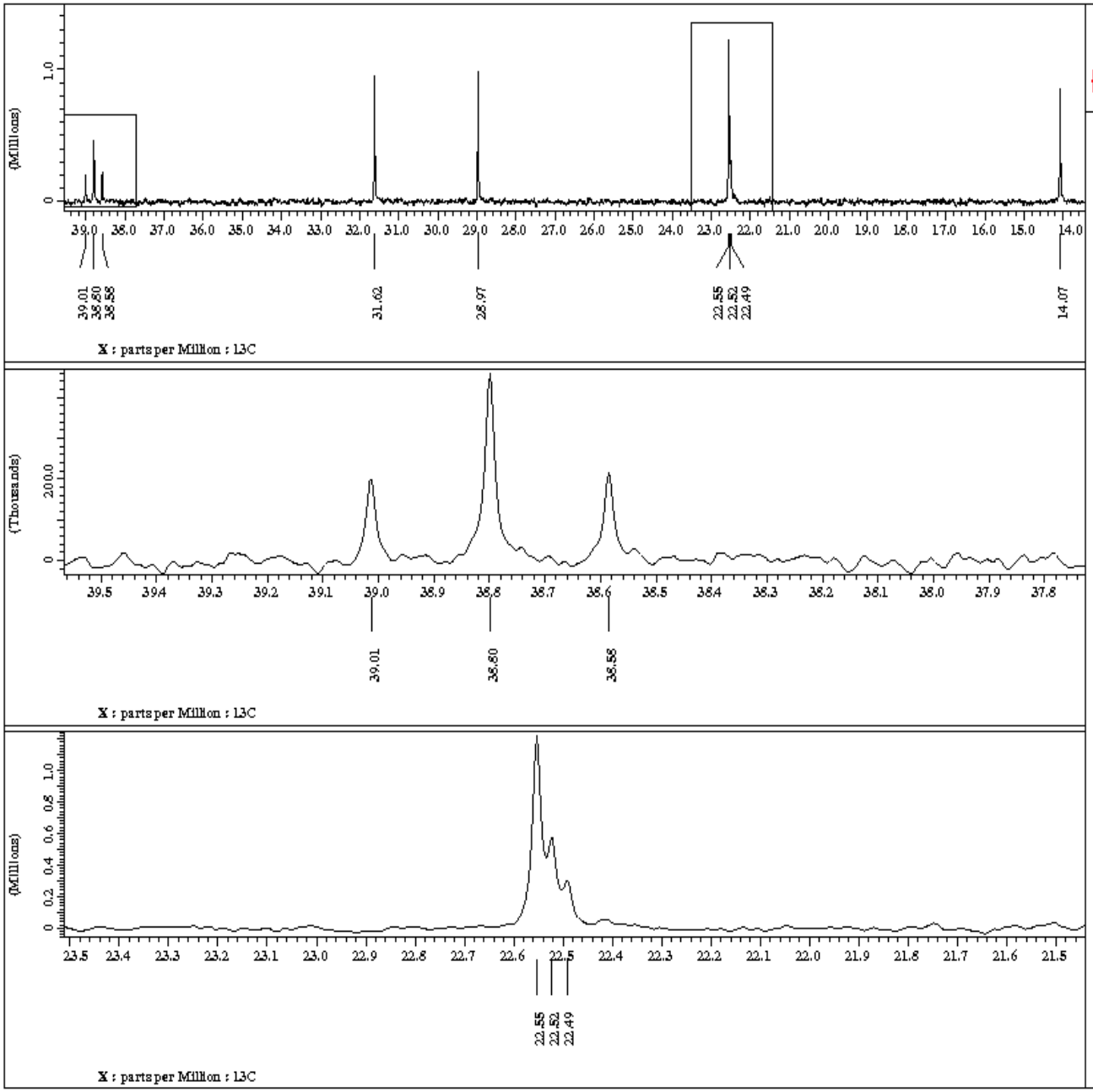
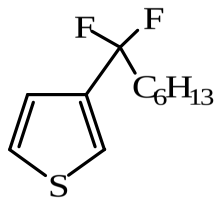


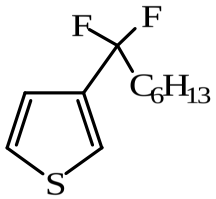
JEOL

Filename	= 1,1-di-F-H-Th-4.jdf
Author	= delta
Experiment	= single_pulse_dec
Sample_id	= S#608687
Solvent	= CHLOROFORM-D
Creation_time	= 29-OCT-2005 10:58:19
Revision_time	= 14-NOV-2008 19:43:38
Current_time	= 14-NOV-2008 19:50:39
Comment	= Single Pulse with Bro
Data_format	= 1D COMPLEX
Dim_size	= 65536
Dim_title	= 13C
Dim_units	= [ppm]
Dimensions	= X
Site	= Eclipse+ 500
Spectrometer	= DELTA_NMR
Field_strength	= 11.7473579[T] (500[MH
X_acq_duration	= 2.0840448[s]
X_domain	= 13C
X_freq	= 125.76529768[MHz]
X_offset	= 100[ppm]
X_points	= 65536
X_prescans	= 4
X_resolution	= 0.47983613[Hz]
X_sweep	= 31.44654088[kHz]
Irr_domain	= 1H
Irr_freq	= 500.15991521[MHz]
Irr_offset	= 5[ppm]
Clipped	= FALSE
Mod_return	= 1
Scans	= 500
Total_scans	= 500
X_90_width	= 14.2[us]
X_acq_time	= 2.0840448[s]
X_angle	= 30[deg]
X_pulse	= 4.73333333[us]
Initial_wait	= 1[s]
Phase_preset	= 3[us]
Recvr_gain	= 30
Relaxation_delay	= 3[s]
Temp_get	= 28.3[dC]
Unblank_time	= 2[us]

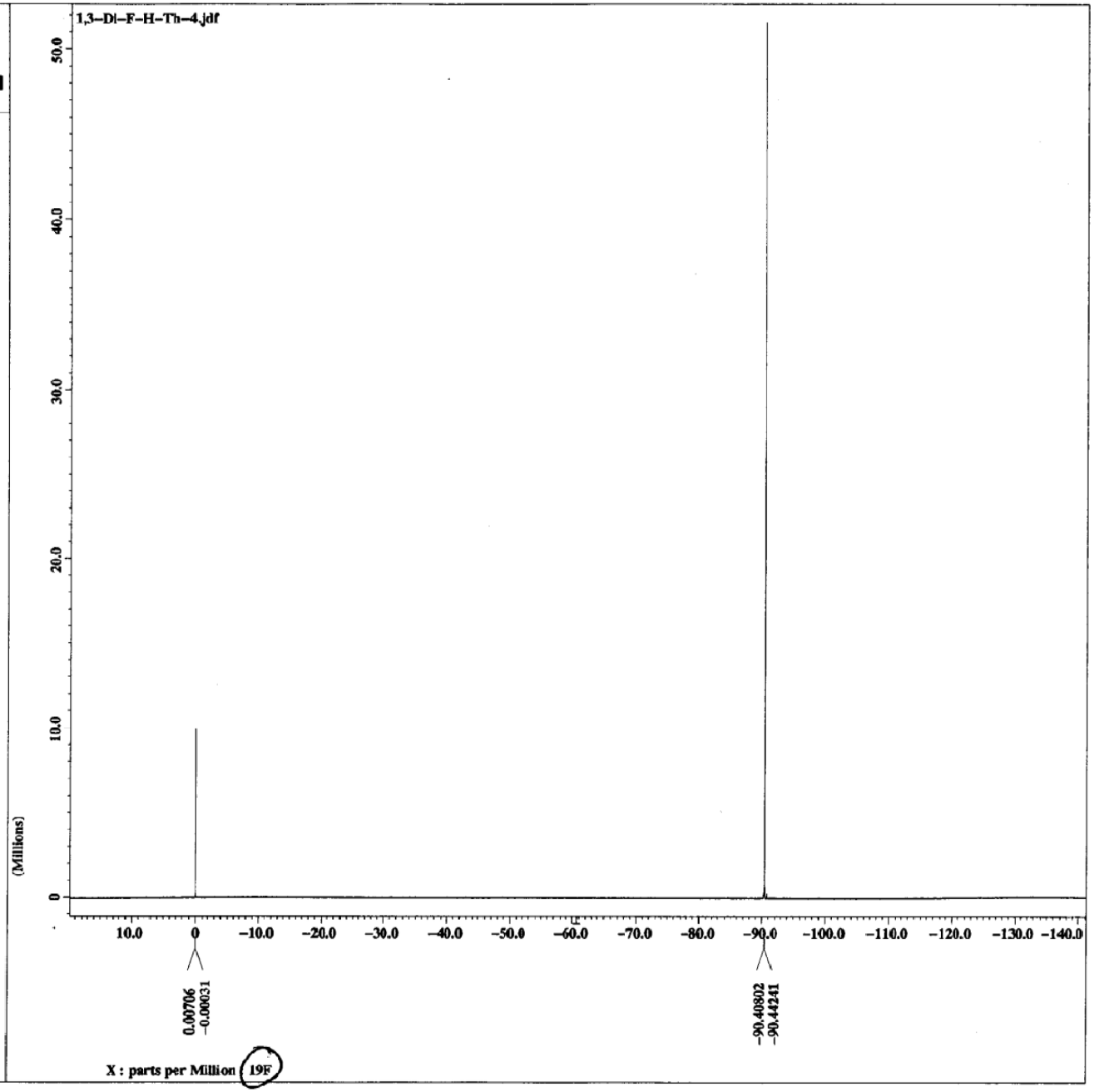


72

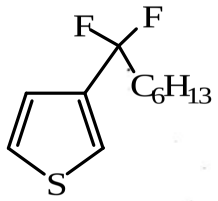
Filename	= 1,3-Di-F-H-Th-4.jdf
Author	= delta
Experiment	= single_pulse.exp
Sample_id	= S#773039
Solvent	= CHLOROFORM-D
Creation_time	= 30-OCT-2005 22:53:53
Revision_time	= 30-OCT-2005 21:34:45
Current_time	= 30-OCT-2005 21:35:32
Content	= Single Pulse Experime
Data_format	= 1D COMPLEX
Dim_size	= 65536
Dim_title	= 19F
Dim_units	= [ppm]
Dimensions	= X
Site	= Eclipse+ 500
Spectrometer	= DELTA_NMR
Field_strength	= 11.7473579[T] (500[MH
X_acq_duration	= 0.8650752[s]
X_domain	= 19F
X_freq	= 470.62046084[MHz]
X_offset	= -60[ppm]
X_points	= 65536
X_prescans	= 0
X_resolution	= 1.15596887[Hz]
X_sweep	= 75.75757576[kHz]
Clipped	= FALSE
Mod_return	= 1
Scans	= 12
Total_scans	= 12
X_90_width	= 16[us]
X_acq_time	= 0.8650752[s]
X_angle	= 45[deg]
X_pulse	= 8[us]
Initial_wait	= 1[s]
Phase_preset	= 3[us]
Recvr_gain	= 22
Relaxation_delay	= 14[s]
Temp_get	= 25.6[dC]
Unblank_time	= 2[us]



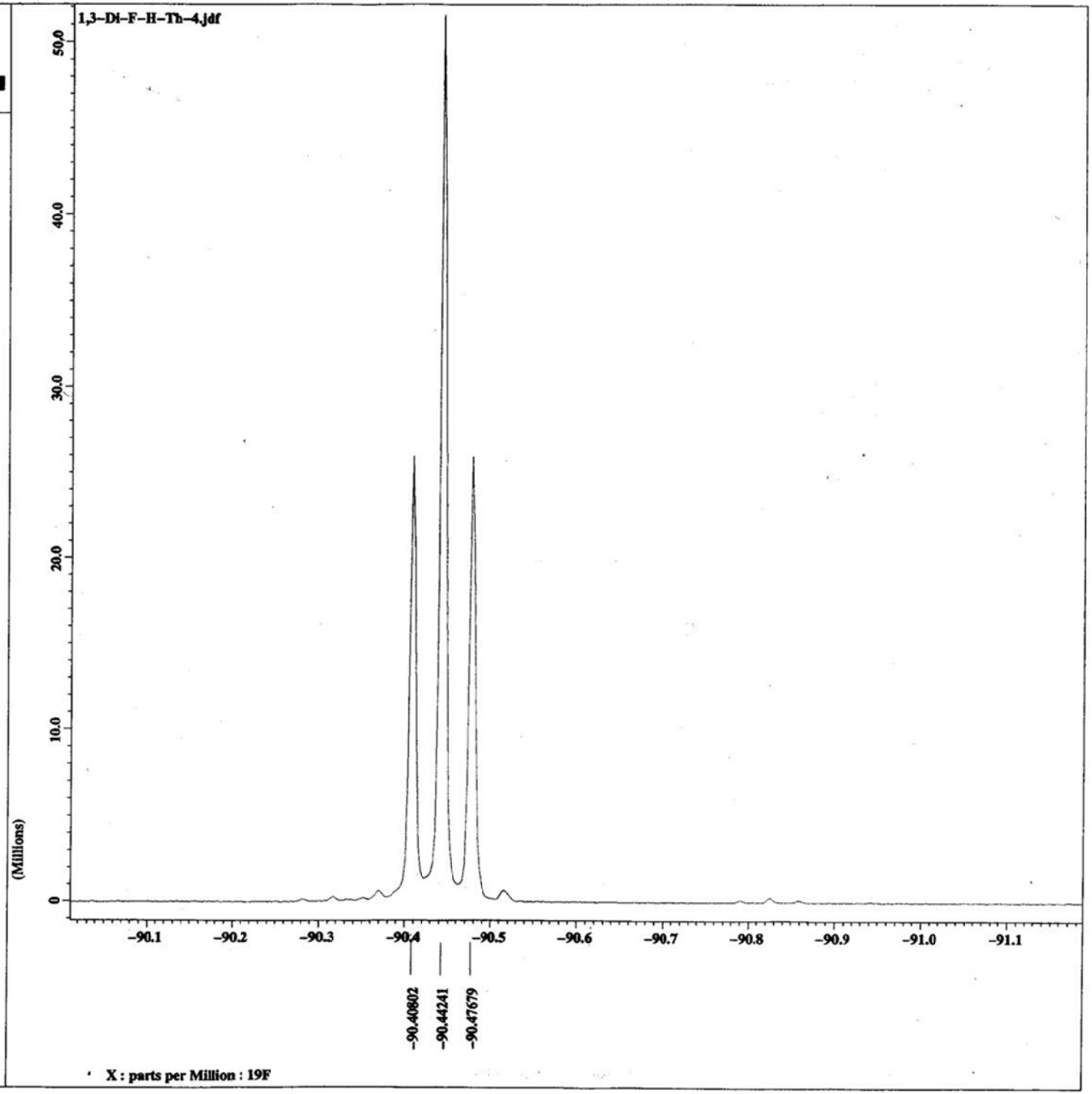
72



Filename	= 1,3-Di-F-H-Th-4.jdf
Author	= delta
Experiment	= single_pulse.exp
Sample_id	= S#773039
Solvent	= CHLOROFORM-D
Creation_time	= 30-OCT-2005 22:53:53
Revision_time	= 30-OCT-2005 21:34:45
Current_time	= 30-OCT-2005 21:35:00
Content	= Single Pulse Experime
Data_format	= 1D COMPLEX
Dim_size	= 65536
Dim_title	= 19F
Dim_units	= [ppm]
Dimensions	= X
Site	= Eclipse+ 500
Spectrometer	= DELTA_NMR
Field_strength	= 11.7473579[T] (500[MH
X_acq_duration	= 0.8650752[s]
X_domain	= 19F
X_freq	= 470.62046084[MHz]
X_offset	= -60[ppm]
X_points	= 65536
X_prescans	= 0
X_resolution	= 1.15596887[Hz]
X_sweep	= 75.75757576[kHz]
Clipped	= FALSE
Mod_return	= 1
Scans	= 12
Total_scans	= 12
X_90_width	= 16[us]
X_acq_time	= 0.8650752[s]
X_angle	= 45[deg]
X_pulse	= 8[us]
Initial_wait	= 1[s]
Phase_preset	= 3[us]
Recvr_gain	= 22
Relaxation_delay	= 14[s]
Temp_get	= 25.6[dC]
Unblank_time	= 2[us]

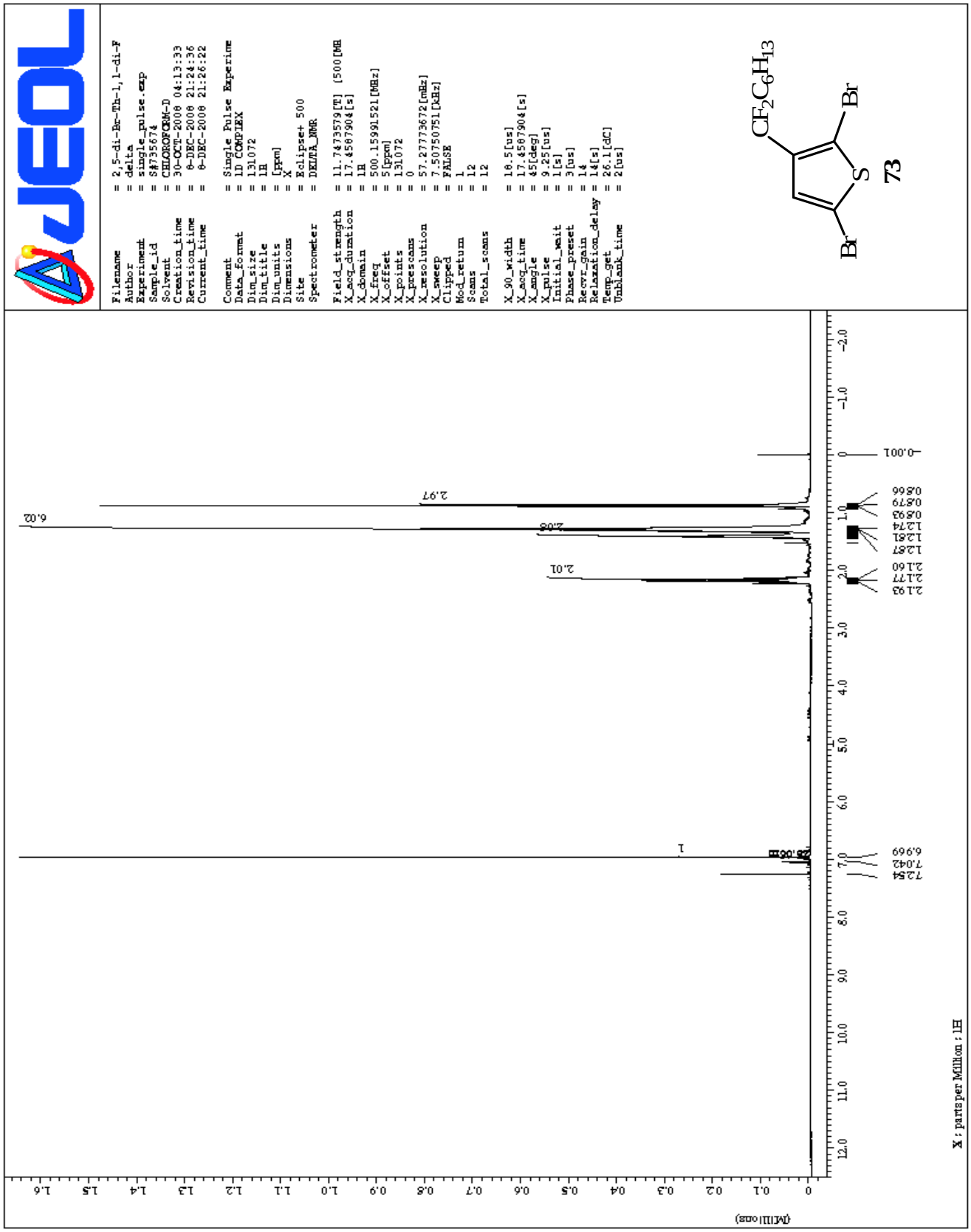


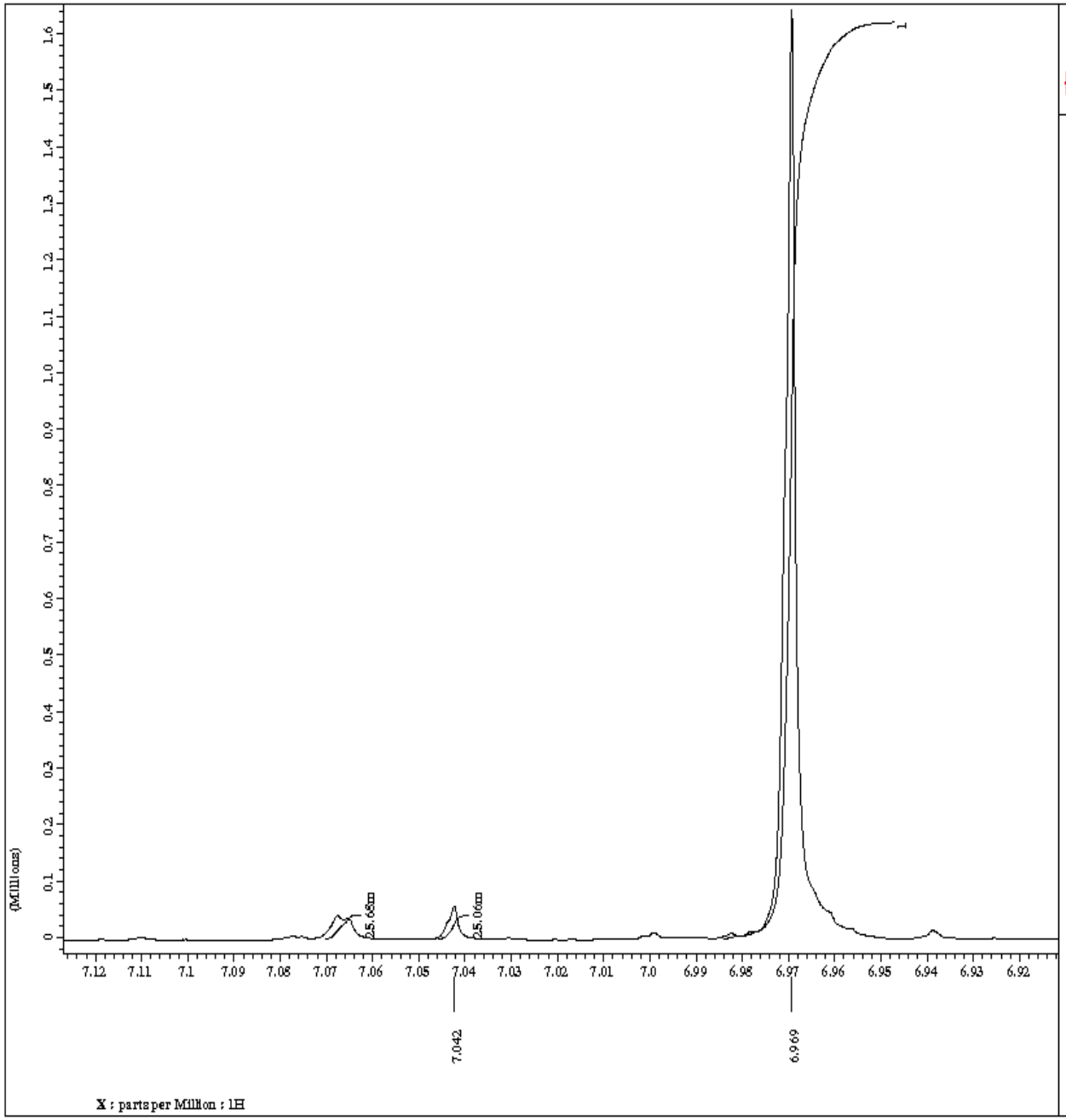
72



APPENDIX 5

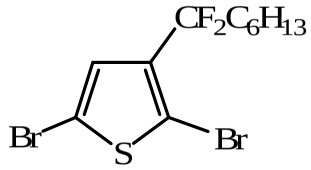
^{1}H, ^{13}C, ^{19}F NMR and IR spectra of 2,5-dibromo-3-(1,1-difluoroheptyl)thiophene (**73**)


Filename = 2,5-di-Br-Th-1,1-di-F
Author = delta
Experiment = single_pulse.exp
Sample_id = S#735674
Solvent = CHLOROFORM-D
Creation_time = 30-OCT-2008 04:13:33
Revision_time = 6-DEC-2008 21:24:36
Current_time = 6-DEC-2008 21:26:22
Comment = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 131072
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DEUTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 17.4587904[s]
X_domain = 1H
X_freq = 500.159915211[MHz]
X_offset = 5[ppm]
X_points = 131072
X_prescans = 0
X_resolution = 57.27773672[mHz]
X_sweep = 7.50750751[kHz]
Clipped = FALSE
Mod_return = 1
Scans = 12
Total_scans = 12
X_90_width = 18.5[us]
X_acq_time = 17.4587904[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 14
Relaxation_delay = 14[s]
Temp_get = 26.1[dC]
Unblank_time = 2[us]
$CF_2C_6H_{13}$
Br
S
Br
73
6.02
2.97
2.08
2.01
1
7.254
7.042
6.969
2.193
2.177
2.160
1.287
1.261
1.274
0.893
0.879
0.866
0.001
X : parts per Million : 1H

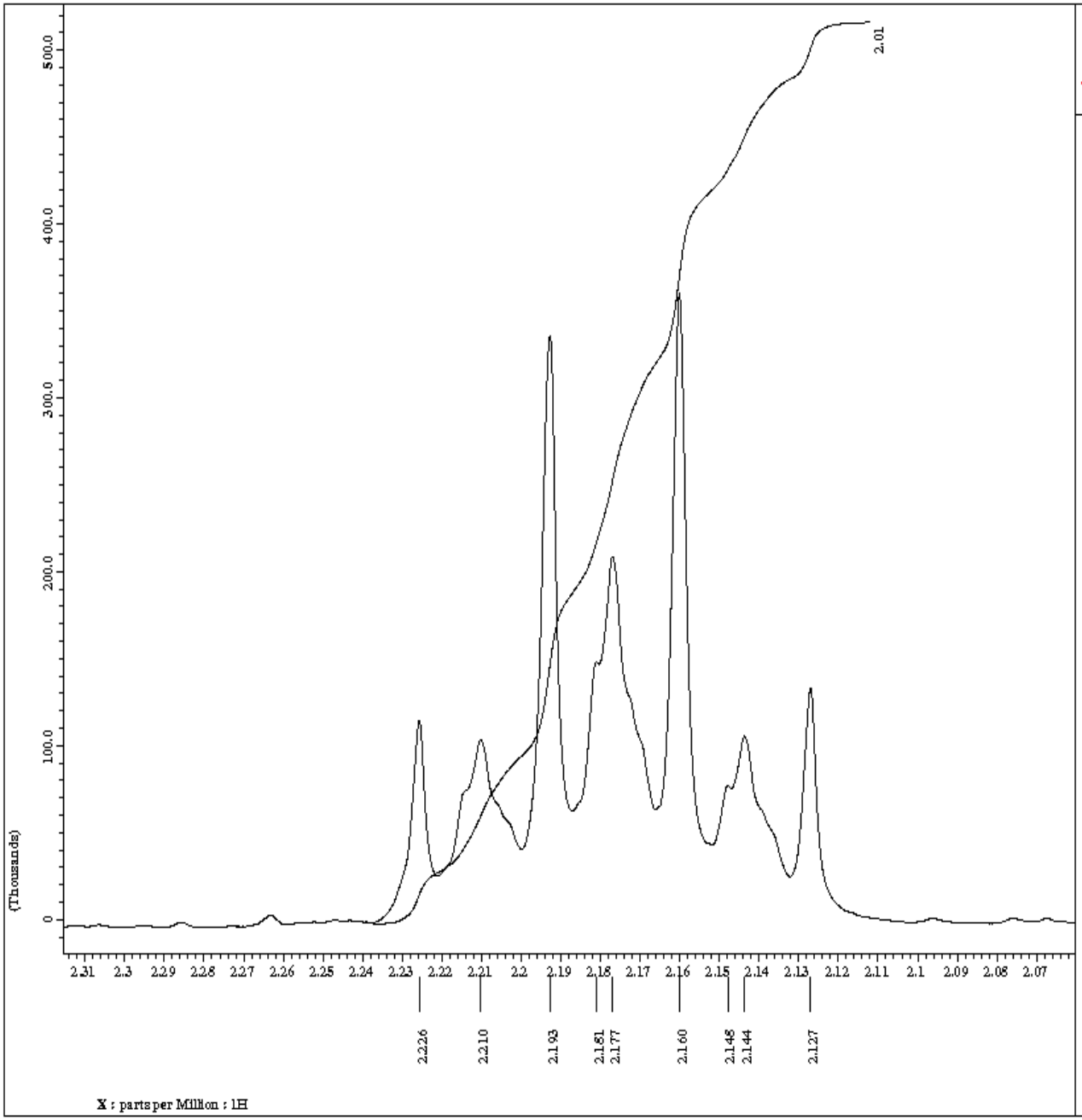


JEOL

Filename	= 2,5-di-Br-Th-1,1-di-F
Author	= delta
Experiment	= single_pulse.exp
Sample_id	= S#735674
Solvent	= CHLOROFORM-D
Creation_time	= 30-OCT-2008 04:13:33
Revision_time	= 8-DEC-2008 21:24:36
Current_time	= 8-DEC-2008 21:24:59
Comment	= Single Pulse Experime
Data_format	= 1D COMPLEX
Dim_size	= 131072
Dim_title	= 1H
Dim_units	= [ppm]
Dimensions	= X
Site	= Eclipse+ 500
Spectrometer	= DELTA_NMR
Field_strength	= 11.7473579[T] (500[MH
X_acq_duration	= 17.4587904[s]
X_domain	= 1H
X_freq	= 500.15991521[MHz]
X_offset	= 5[ppm]
X_points	= 131072
X_prescans	= 0
X_resolution	= 57.27773672[mHz]
X_sweep	= 7.50750751[kHz]
Clipped	= FALSE
Mod_return	= 1
Scans	= 12
Total_scans	= 12
X_90_width	= 10.5[us]
X_acq_time	= 17.4587904[s]
X_angle	= 45[deg]
X_pulse	= 9.25[us]
Initial_wait	= 1[s]
Phase_preset	= 3[us]
Recvr_gain	= 14
Relaxation_delay	= 14[s]
Temp_get	= 26.1[dC]
Unblank_time	= 2[us]



73



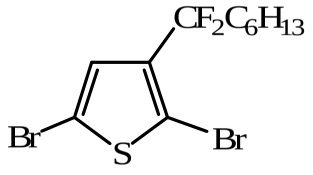
JEOL

```
Filename          = 2,5-di-Br-Th-1,1-di-F
Author            = delta
Experiment        = single_pulse.exp
Sample_id         = S#735674
Solvent           = CHLOROFORM-D
Creation_time     = 30-OCT-2008 04:13:33
Revision_time     =  8-DEC-2008 21:24:36
Current_time      =  8-DEC-2008 21:29:07

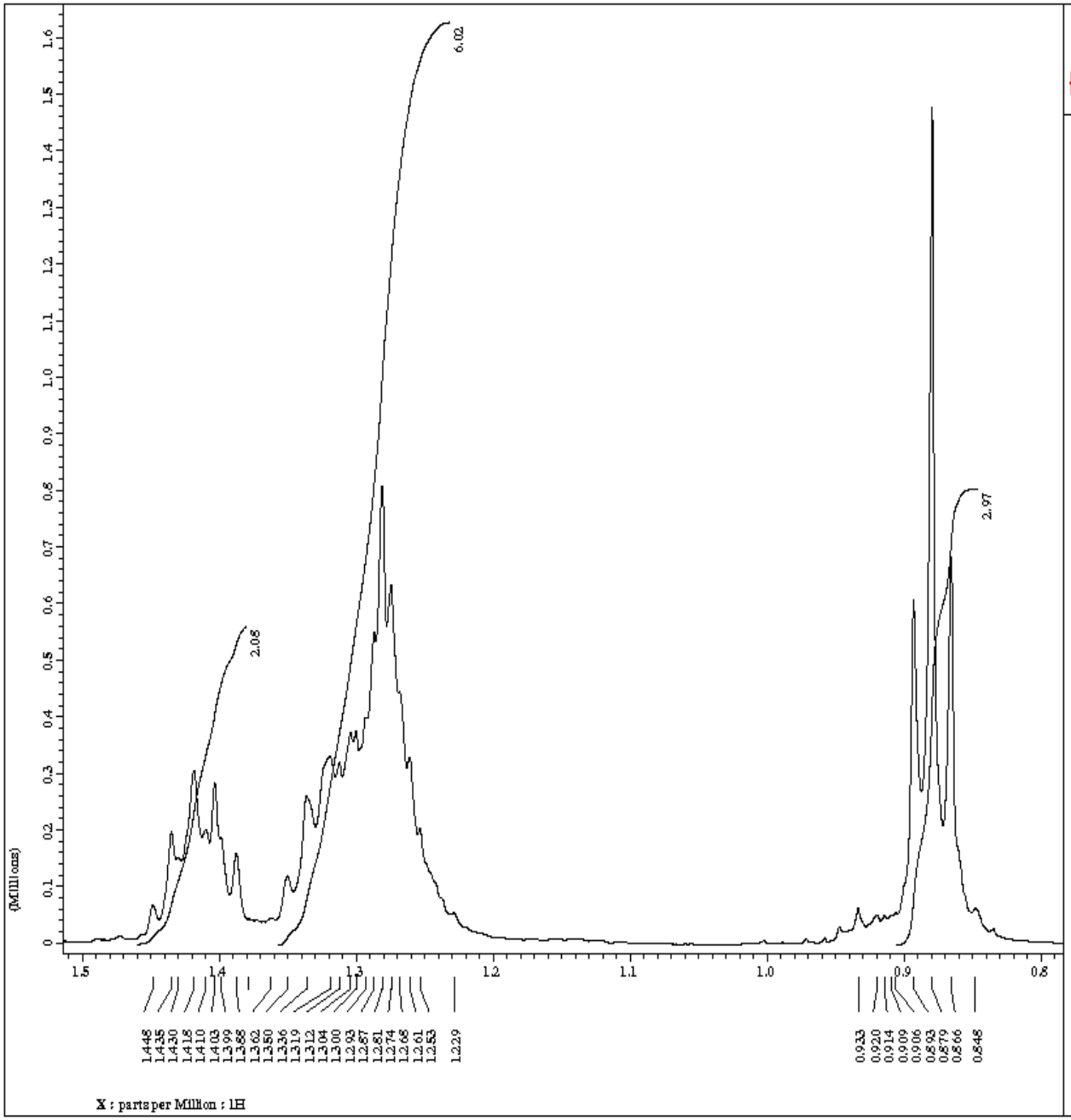
Comment           = Single Pulse Experime
Data_format       = 1D COMPLEX
Dim_size          = 131072
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

Field_strength    = 11.7473579[T]  (500[MH
X_acq_duration    = 17.4587904[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 5[ppm]
X_points          = 131072
X_prescans        = 0
X_resolution      = 57.27773672[mHz]
X_sweep           = 7.50750751[kHz]
Clipped           = FALSE
Mod_return        = 1
Scans             = 12
Total_scans       = 12

X_90_width        = 10.5[us]
X_acq_time        = 17.4587904[s]
X_angle           = 45[deg]
X_pulse           = 9.25[us]
Initial_wait      = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 14
Relaxation_delay  = 14[s]
Temp_get          = 26.1[dC]
Unblank_time      = 2[us]
```



73



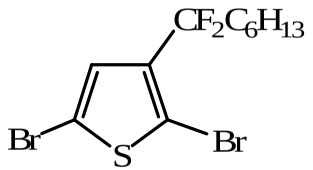
JEOL

Filename = 2,5-di-Br-Th-1,1-di-F
Author = delta
Experiment = single_pulse.exp
Sample_id = S#735674
Solvent = CHLOROFORM-D
Creation_time = 30-OCT-2008 04:13:33
Revision_time = 8-DEC-2008 21:24:36
Current_time = 8-DEC-2008 21:31:36

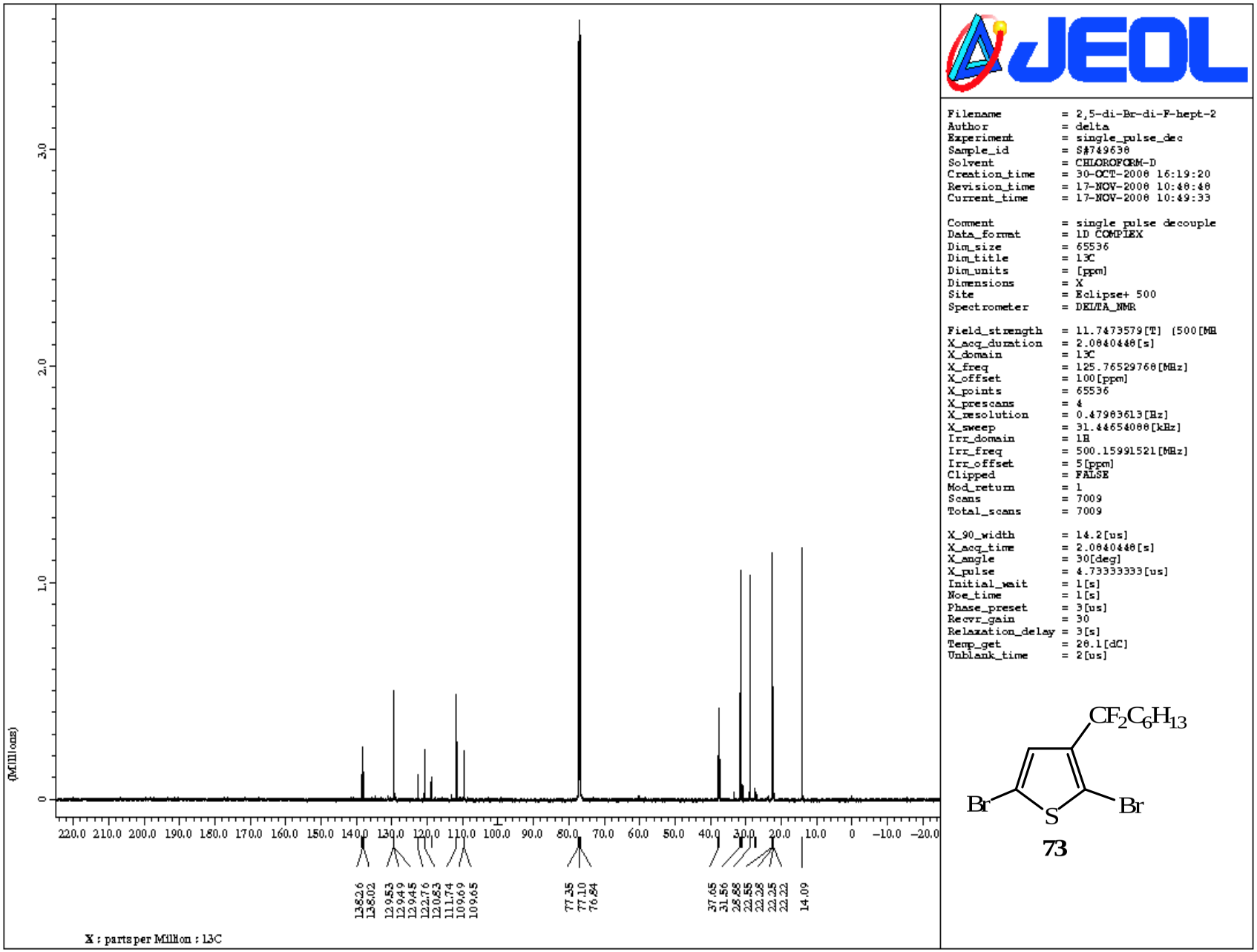
Comment = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 131072
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR

Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 17.4587904[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 131072
X_prescans = 0
X_resolution = 57.27773672[mHz]
X_sweep = 7.50750751[kHz]
Clipped = FALSE
Mod_return = 1
Scans = 12
Total_scans = 12

X_90_width = 18.5[us]
X_acq_time = 17.4587904[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 14
Relaxation_delay = 14[s]
Temp_get = 26.1[dC]
Unblank_time = 2[us]



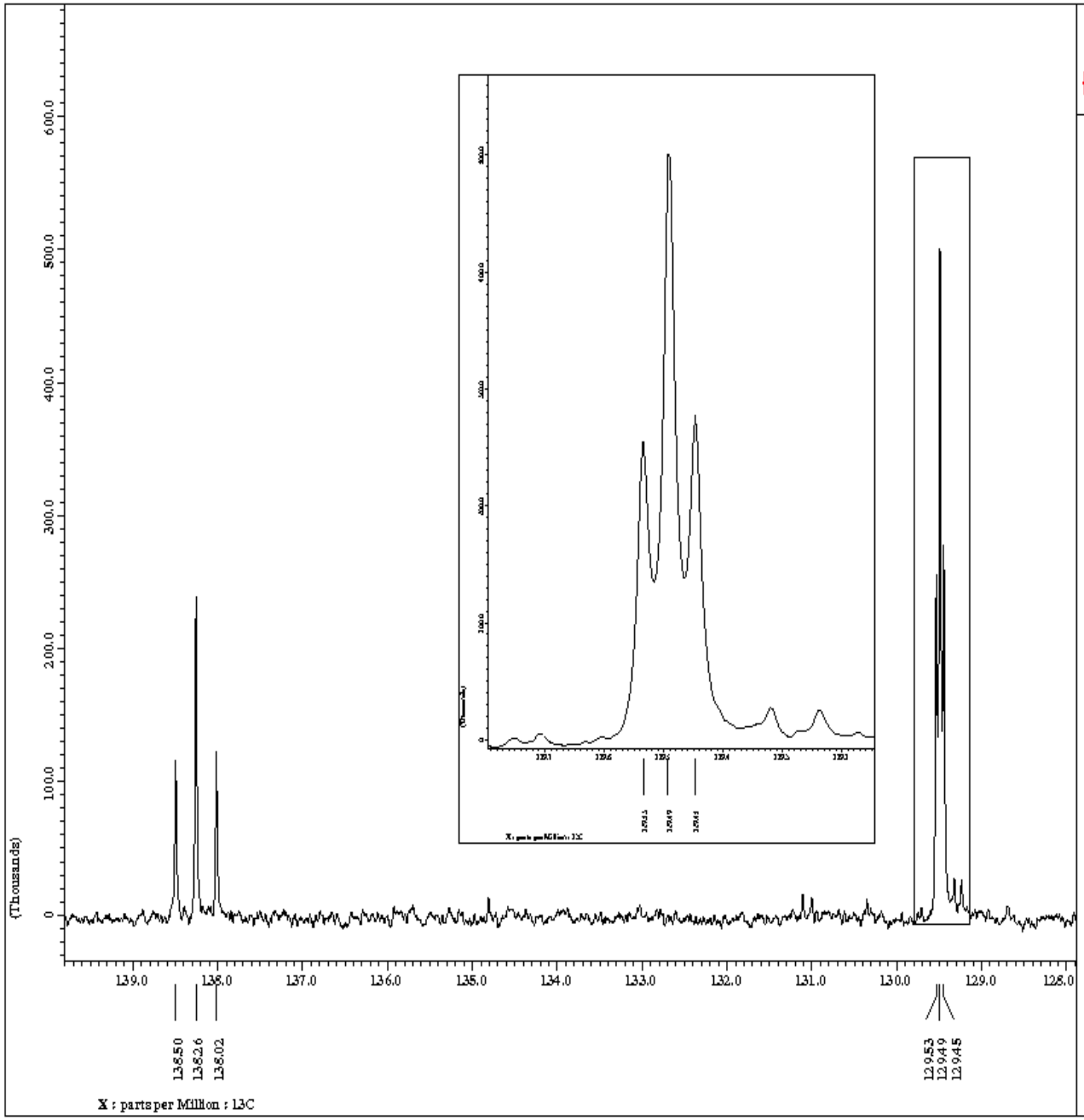
73



JEOL

Filename	= 2,5-di-Br-di-F-hept-2
Author	= delta
Experiment	= single_pulse_dec
Sample_id	= S#749630
Solvent	= CHLOROFORM-D
Creation_time	= 30-OCT-2008 16:19:20
Revision_time	= 17-NOV-2008 10:48:48
Current_time	= 17-NOV-2008 10:49:33
Comment	= single pulse decouple
Data_format	= 1D COMPLEX
Dim_size	= 65536
Dim_title	= 13C
Dim_units	= [ppm]
Dimensions	= X
Site	= Eclipse+ 500
Spectrometer	= DELTA_NMR
Field_strength	= 11.7473579[T] (500[MH
X_acq_duration	= 2.0840448[s]
X_domain	= 13C
X_freq	= 125.76529768[MHz]
X_offset	= 100[ppm]
X_points	= 65536
X_prescans	= 4
X_resolution	= 0.47983613[Hz]
X_sweep	= 31.44654088[kHz]
Irr_domain	= 1H
Irr_freq	= 500.15991521[MHz]
Irr_offset	= 5[ppm]
Clipped	= FALSE
Mod_return	= 1
Scans	= 7009
Total_scans	= 7009
X_90_width	= 14.2[us]
X_acq_time	= 2.0840448[s]
X_angle	= 30[deg]
X_pulse	= 4.73333333[us]
Initial_wait	= 1[s]
Noe_time	= 1[s]
Phase_preset	= 3[us]
Recvr_gain	= 30
Relaxation_delay	= 3[s]
Temp_get	= 20.1[dC]
Unblank_time	= 2[us]

73

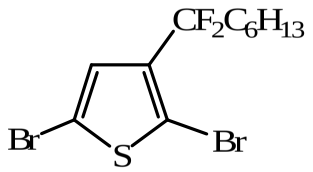


Filename = 2,5-di-Br-di-F-hept-4
Author = delta
Experiment = single_pulse_dec
Sample_id = S#749630
Solvent = CHLOROFORM-D
Creation_time = 30-OCT-2008 16:19:20
Revision_time = 17-NOV-2008 10:50:45
Current_time = 17-NOV-2008 10:56:04

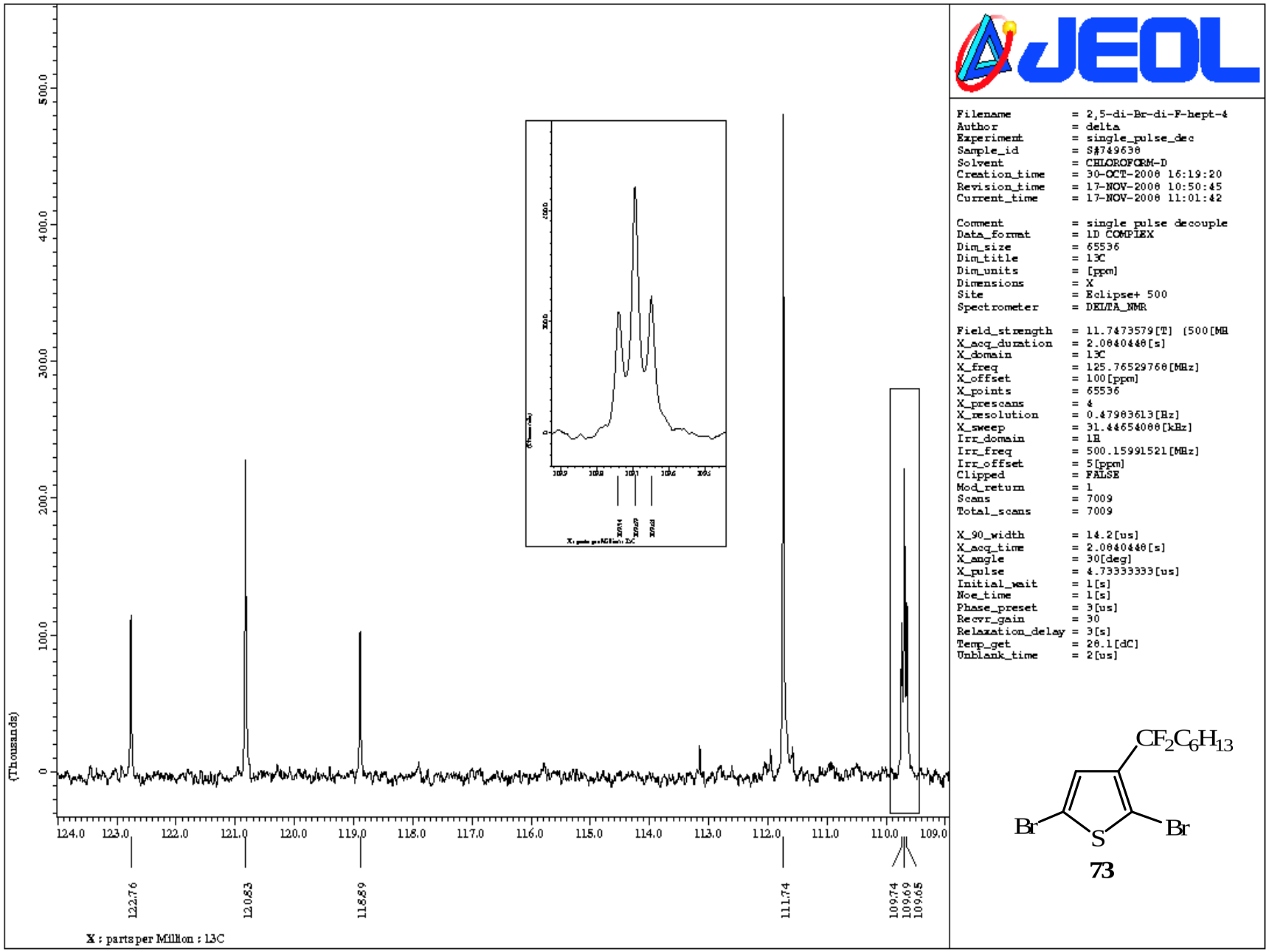
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 65536
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR

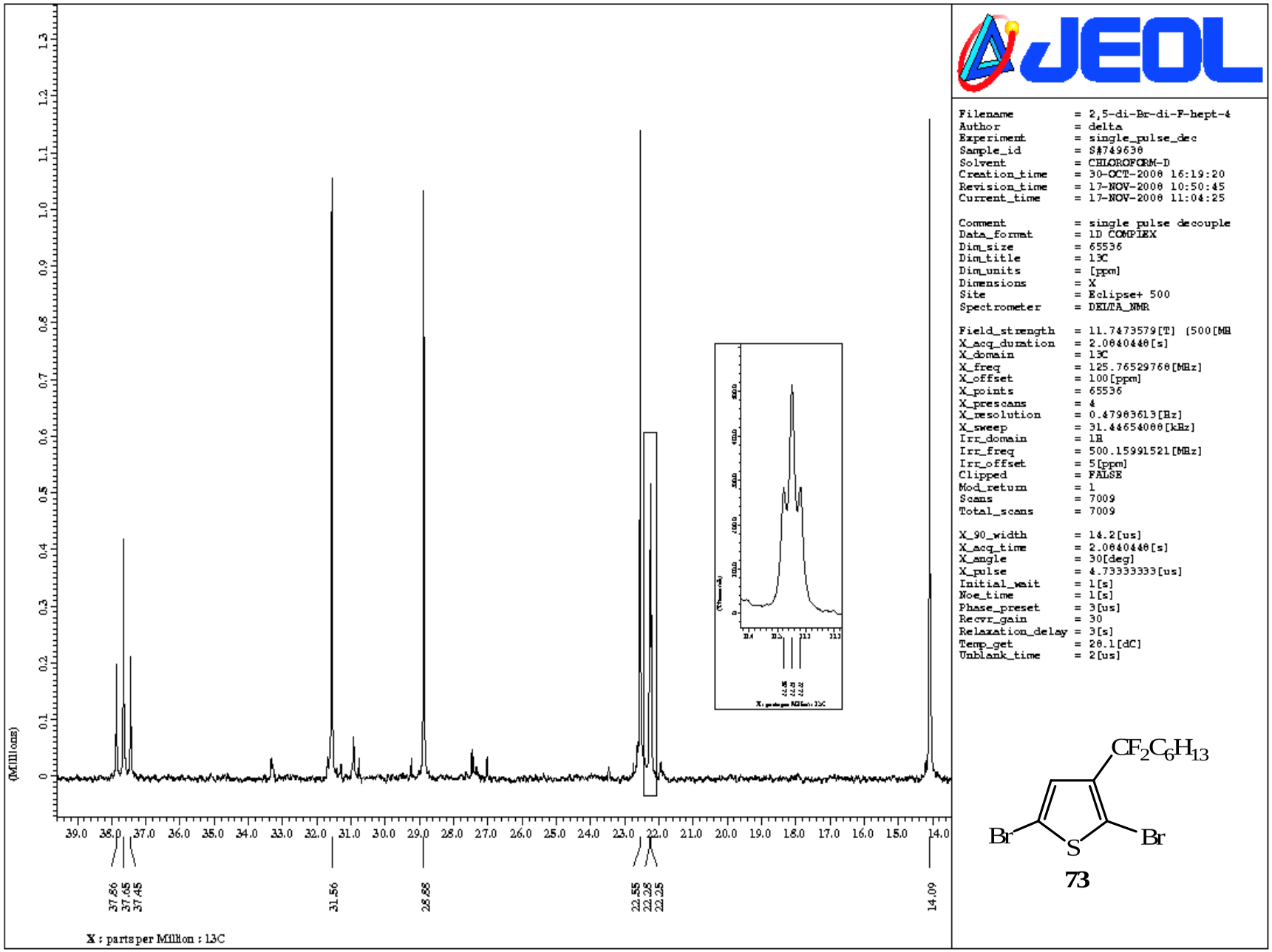
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.0840448[s]
X_domain = 13C
X_freq = 125.76529768[MHz]
X_offset = 100[ppm]
X_points = 65536
X_prescans = 4
X_resolution = 0.47983613[Hz]
X_sweep = 31.44654088[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 7009
Total_scans = 7009

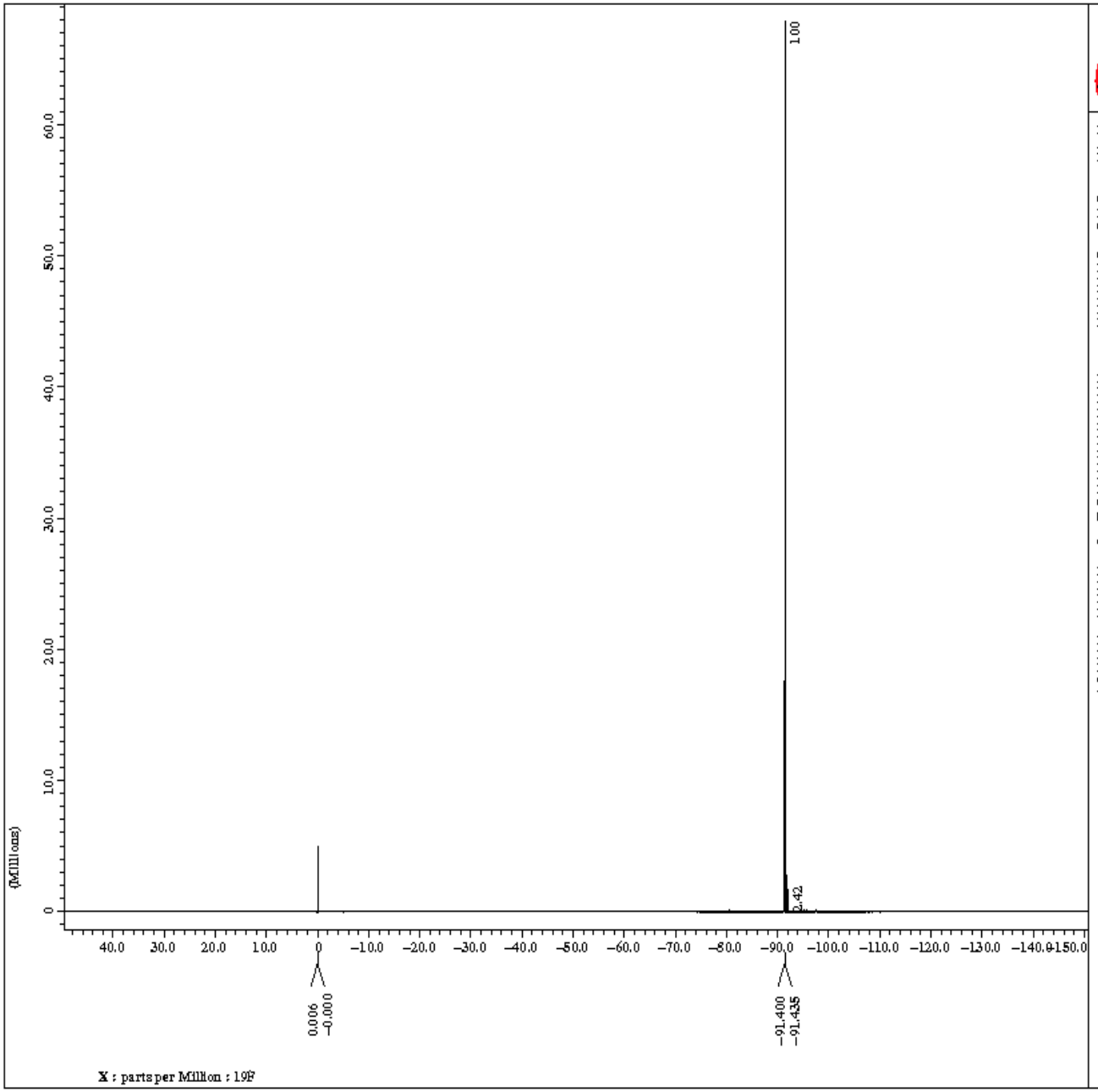
X_90_width = 14.2[us]
X_acq_time = 2.0840448[s]
X_angle = 30[deg]
X_pulse = 4.73333333[us]
Initial_wait = 1[s]
Noe_time = 1[s]
Phase_preset = 3[us]
Recvr_gain = 30
Relaxation_delay = 3[s]
Temp_get = 28.1[dC]
Unblank_time = 2[us]



73

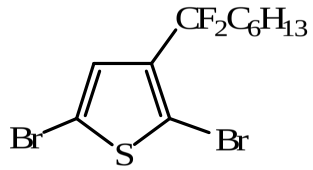

JEOL
Filename = 2,5-di-Br-di-F-hept-4
Author = delta
Experiment = single_pulse_dec
Sample_id = S#749630
Solvent = CHLOROFORM-D
Creation_time = 30-OCT-2008 16:19:20
Revision_time = 17-NOV-2008 10:50:45
Current_time = 17-NOV-2008 11:01:42
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 65536
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.0840448[s]
X_domain = 13C
X_freq = 125.76529768[MHz]
X_offset = 100[ppm]
X_points = 65536
X_prescans = 4
X_resolution = 0.47983613[Hz]
X_sweep = 31.44654088[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 7009
Total_scans = 7009
X_90_width = 14.2[us]
X_acq_time = 2.0840448[s]
X_angle = 30[deg]
X_pulse = 4.73333333[us]
Initial_wait = 1[s]
Noe_time = 1[s]
Phase_preset = 3[us]
Recvr_gain = 30
Relaxation_delay = 3[s]
Temp_get = 28.1[dC]
Unblank_time = 2[us]
(Thousands)
500.0
400.0
300.0
200.0
100.0
0
124.0 123.0 122.0 121.0 120.0 119.0 118.0 117.0 116.0 115.0 114.0 113.0 112.0 111.0 110.0 109.0
122.76
120.83
118.89
111.74
109.74
109.69
109.65
X : parts per Million : 13C
CF2C6H13
Br
S
Br
73


(Millions)
39.0 38.0 37.0 36.0 35.0 34.0 33.0 32.0 31.0 30.0 29.0 28.0 27.0 26.0 25.0 24.0 23.0 22.0 21.0 20.0 19.0 18.0 17.0 16.0 15.0 14.0
37.56
37.65
37.45
31.56
28.88
22.55
22.28
22.25
14.09
X : parts per Million : 13C
Filename = 2,5-di-Br-di-F-hept-4
Author = delta
Experiment = single_pulse_dec
Sample_id = S#749630
Solvent = CHLOROFORM-D
Creation_time = 30-OCT-2008 16:19:20
Revision_time = 17-NOV-2008 10:50:45
Current_time = 17-NOV-2008 11:04:25
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 65536
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.0840448[s]
X_domain = 13C
X_freq = 125.76529768[MHz]
X_offset = 100[ppm]
X_points = 65536
X_prescans = 4
X_resolution = 0.47903613[Hz]
X_sweep = 31.44654088[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 7009
Total_scans = 7009
X_90_width = 14.2[us]
X_acq_time = 2.0840448[s]
X_angle = 30[deg]
X_pulse = 4.73333333[us]
Initial_wait = 1[s]
Noe_time = 1[s]
Phase_preset = 3[us]
Recvr_gain = 30
Relaxation_delay = 3[s]
Temp_get = 28.1[dC]
Unblank_time = 2[us]
CF2C6H13
Br
S
Br
73

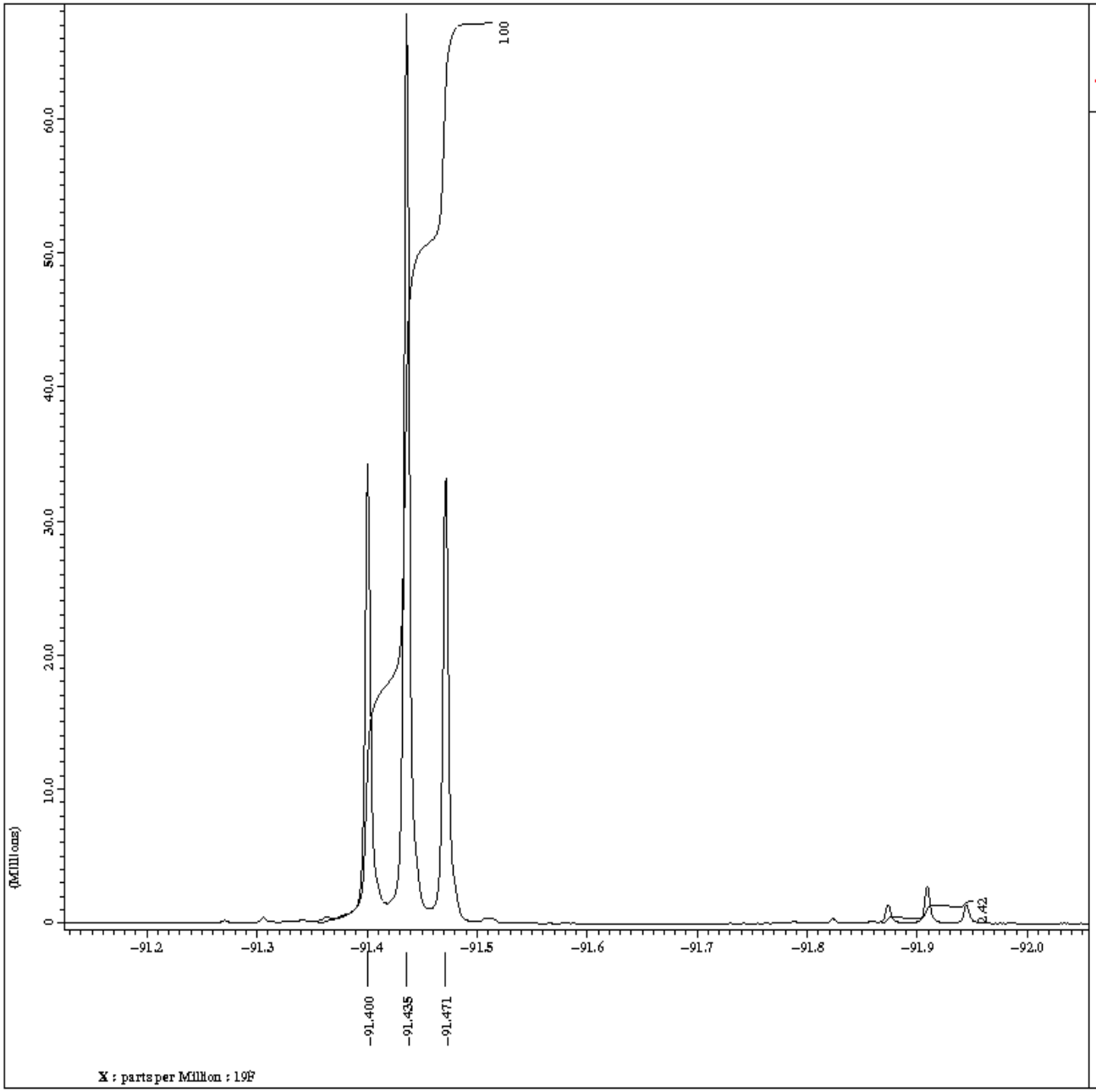


JEOL

Filename	= 2,5-di-Br-di-F-hept-T
Author	= delta
Experiment	= single_pulse.exp
Sample_id	= S#454631
Solvent	= CHLOROFORM-D
Creation_time	= 30-OCT-2008 20:22:33
Revision_time	= 30-OCT-2008 12:52:04
Current_time	= 17-NOV-2008 10:12:52
Comment	= Single Pulse Experime
Data_format	= 1D COMPLEX
Dim_size	= 131072
Dim_title	= 19F
Dim_units	= [ppm]
Dimensions	= X
Site	= Eclipse+ 500
Spectrometer	= DELTA_NMR
Field_strength	= 11.7473579[T] (500[MH
X_acq_duration	= 1.3893632[s]
X_domain	= 19F
X_freq	= 470.62046084[MHz]
X_offset	= −50[ppm]
X_points	= 131072
X_prescans	= 0
X_resolution	= 0.7197542[Hz]
X_sweep	= 94.33962264[kHz]
Clipped	= FALSE
Mod_return	= 1
Scans	= 64
Total_scans	= 64
X_90_width	= 16[us]
X_acq_time	= 1.3893632[s]
X_angle	= 45[deg]
X_pulse	= 8[us]
Initial_wait	= 1[s]
Phase_preset	= 3[us]
Recvr_gain	= 23
Relaxation_delay	= 4[s]
Temp_get	= 25.9[dC]
Unblank_time	= 2[us]



73



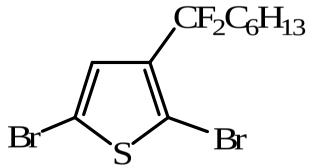
JEOL

```
Filename          = 2,5-di-Br-di-F-hept-T
Author            = delta
Experiment        = single_pulse.exp
Sample_id         = S#454031
Solvent           = CHLOROFORM-D
Creation_time     = 30-OCT-2008 20:22:33
Revision_time     = 30-OCT-2008 12:52:04
Current_time      = 17-NOV-2008 10:14:50

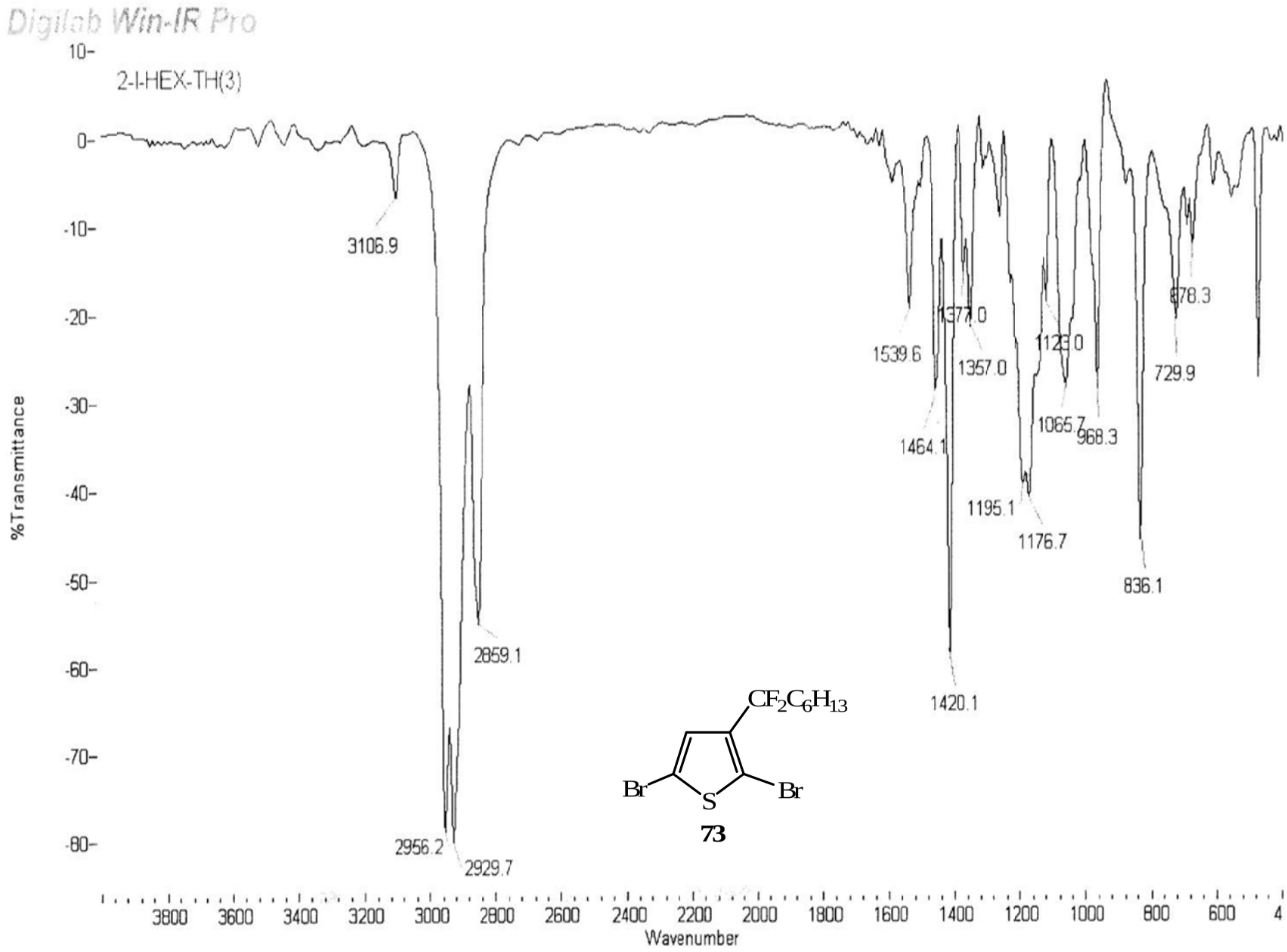
Comment           = Single Pulse Experime
Data_format       = 1D COMPLEX
Dim_size          = 131072
Dim_title         = 19F
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 1.3893632[s]
X_domain          = 19F
X_freq            = 470.62046084[MHz]
X_offset          = -50[ppm]
X_points          = 131072
X_prescans        = 0
X_resolution      = 0.7197542[Hz]
X_sweep           = 94.33962264[kHz]
Clipped           = FALSE
Mod_return        = 1
Scans             = 64
Total_scans       = 64

X_90_width        = 16[us]
X_acq_time        = 1.3893632[s]
X_angle           = 45[deg]
X_pulse           = 8[us]
Initial_wait      = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 23
Relaxation_delay  = 4[s]
Temp_get          = 25.9[dC]
Unblank_time      = 2[us]
```



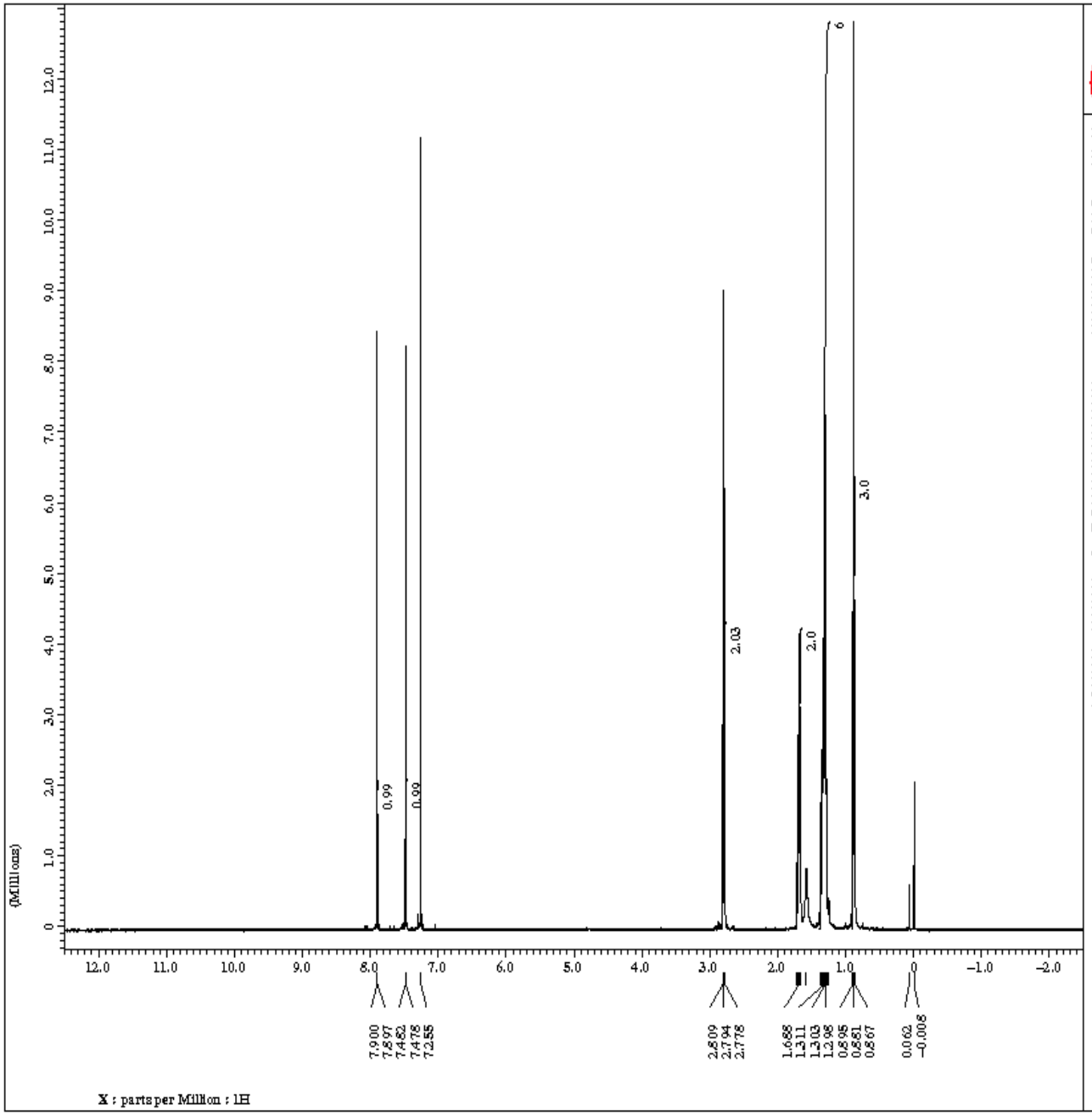
73


Digilab Win-IR Pro
2-I-HEX-TH(3)
%Transmittance
Wavenumber
3106.9
2956.2
2929.7
2859.1
1539.6
1464.1
1420.1
1377.0
1357.0
1195.1
1176.7
1123.0
1065.7
968.3
878.3
836.1
729.9
Br
S
Br
CF2C6H13

73

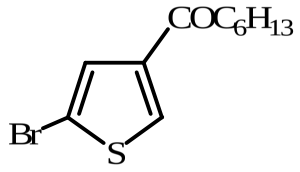
APPENDIX 6

^{1}H, ^{13}C NMR and IR spectra of 5-bromo-3-heptanoylthiophene (**78**)

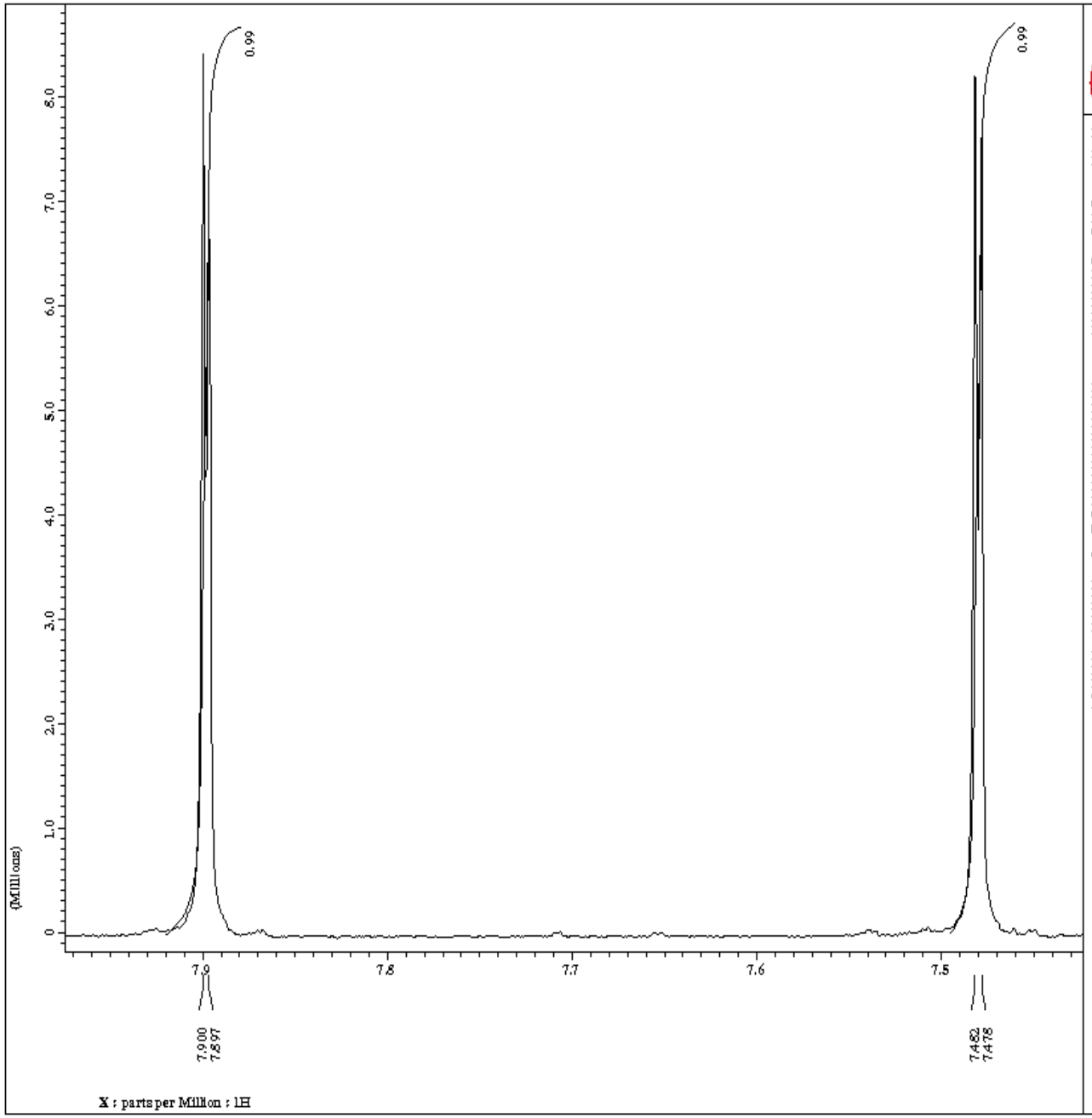


JEOL

Filename	= 5-Br-Hept-Th-3.jdf
Author	= delta
Experiment	= single_pulse.exp
Sample_id	= S#604200
Solvent	= CHLOROFORM-D
Creation_time	= 12-OCT-2008 00:15:52
Revision_time	= 10-DEC-2008 13:01:27
Current_time	= 10-DEC-2008 13:01:43
Comment	= Single Pulse Experime
Data_format	= 1D COMPLEX
Dim_size	= 16384
Dim_title	= 1H
Dim_units	= [ppm]
Dimensions	= X
Site	= Eclipse+ 500
Spectrometer	= DELTA_NMR
Field_strength	= 11.7473579[T] (500[MH
X_acq_duration	= 2.1823488[s]
X_domain	= 1H
X_freq	= 500.15991521[MHz]
X_offset	= 5[ppm]
X_points	= 16384
X_prescans	= 0
X_resolution	= 0.45822189[Hz]
X_sweep	= 7.50750751[kHz]
Clipped	= FALSE
Mod_return	= 1
Scans	= 8
Total_scans	= 8
X_90_width	= 10.5[us]
X_acq_time	= 2.1823488[s]
X_angle	= 45[deg]
X_pulse	= 9.25[us]
Initial_wait	= 1[s]
Phase_preset	= 3[us]
Recvr_gain	= 21
Relaxation_delay	= 4[s]
Temp_get	= 25.8[dC]
Unblank_time	= 2[us]



78



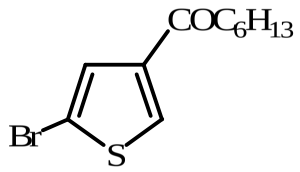
JEOL

```
Filename          = 5-Br-Hept-Th-3.jdf
Author            = delta
Experiment        = single_pulse.exp
Sample_id         = S#604200
Solvent           = CHLOROFORM-D
Creation_time     = 12-OCT-2008 00:15:52
Revision_time     = 10-DEC-2008 13:01:27
Current_time      = 10-DEC-2008 13:02:02

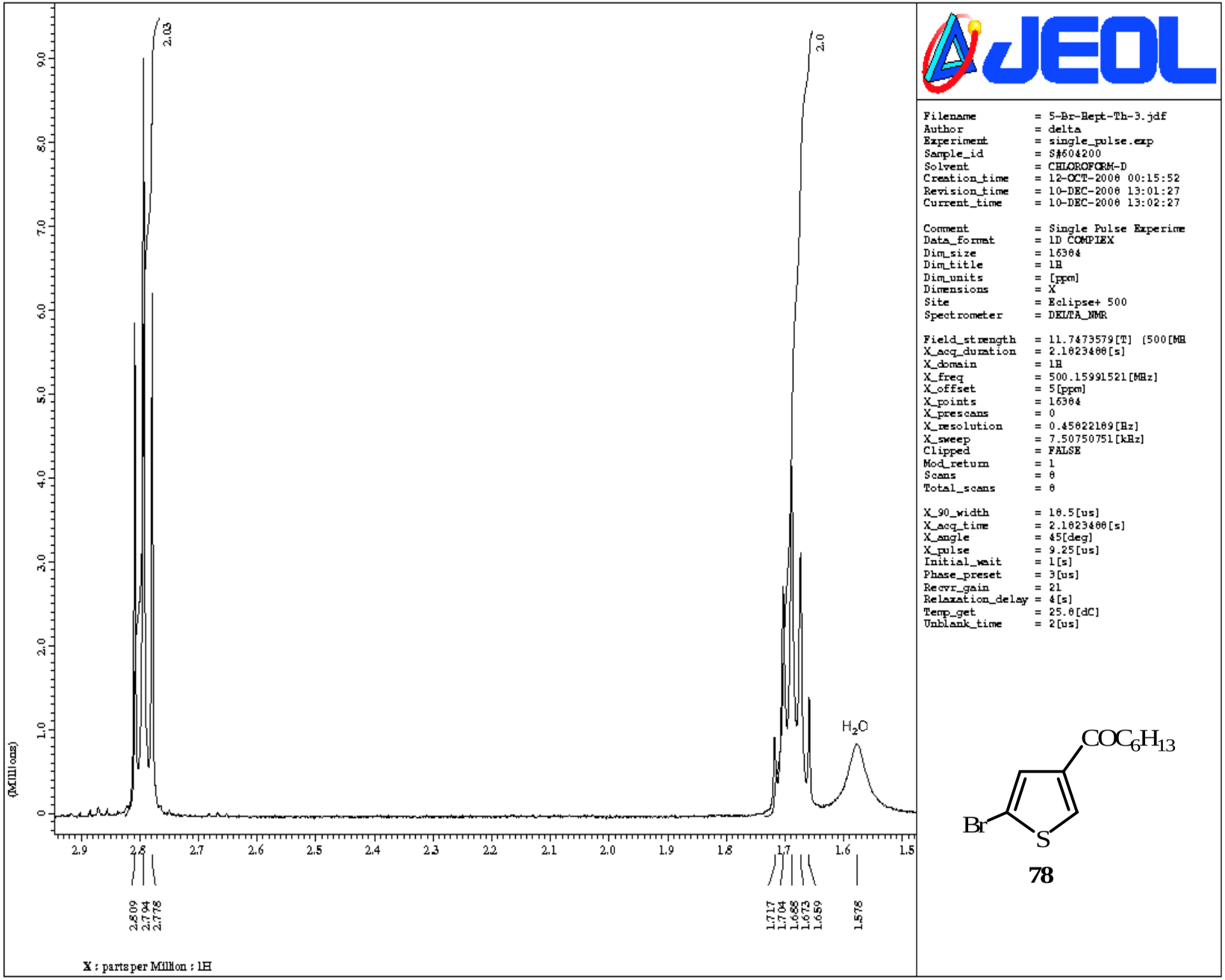
Comment           = Single Pulse Experime
Data_format       = 1D COMPLEX
Dim_size          = 16384
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

Field_strength    = 11.7473579[T]  (500[MH
X_acq_duration    = 2.1823488[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 5[ppm]
X_points          = 16384
X_prescans        = 0
X_resolution      = 0.45822189[Hz]
X_sweep           = 7.50750751[kHz]
Clipped           = FALSE
Mod_return        = 1
Scans             = 8
Total_scans       = 8

X_90_width        = 10.5[us]
X_acq_time        = 2.1823488[s]
X_angle           = 45[deg]
X_pulse           = 9.25[us]
Initial_wait      = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 21
Relaxation_delay  = 4[s]
Temp_get          = 25.8[dC]
Unblank_time      = 2[us]
```



78



JEOL

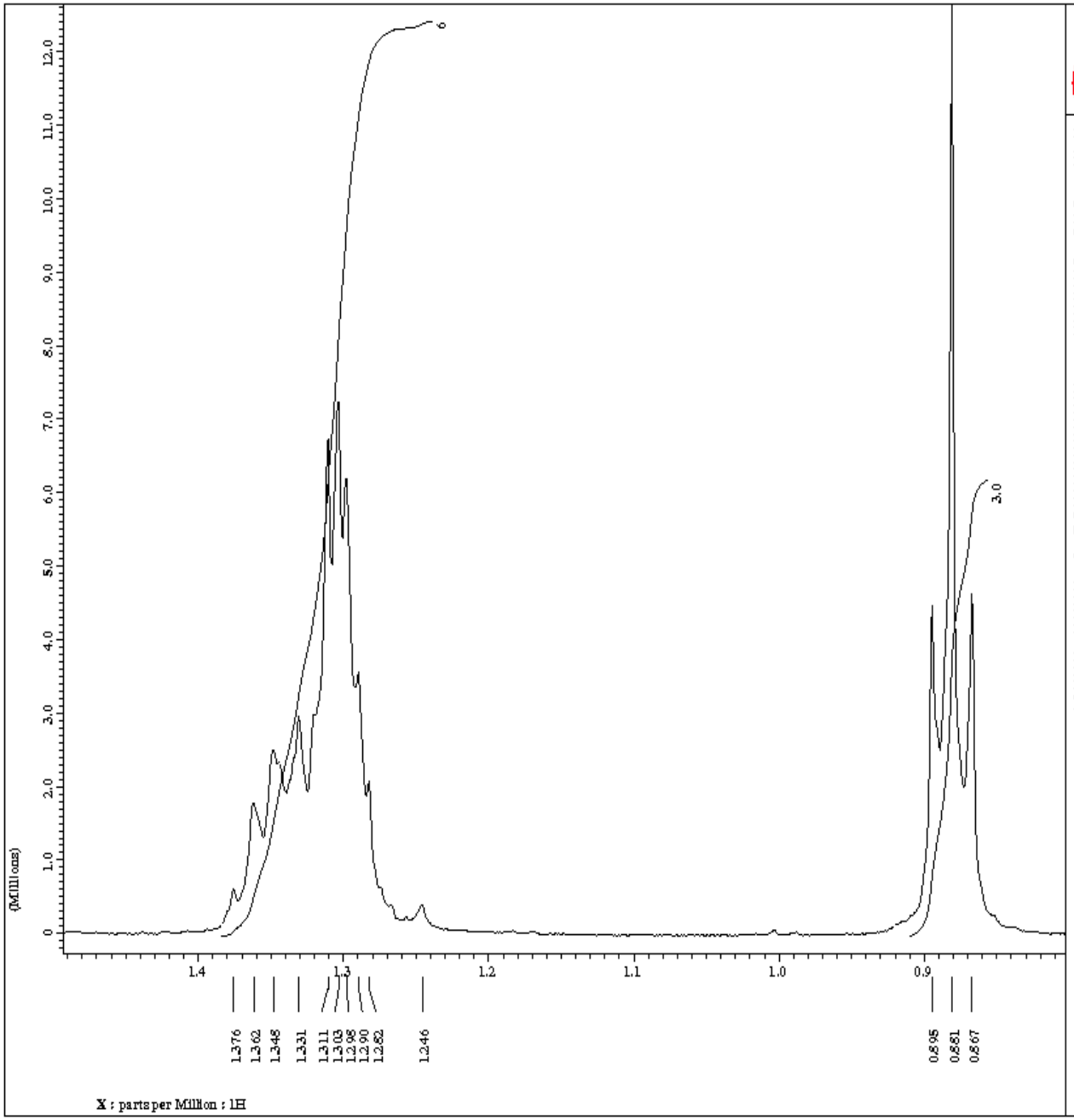
```
Filename          = 5-Br-Hept-Th-3.jdf
Author            = delta
Experiment        = single_pulse.exp
Sample_id         = S#604200
Solvent           = CHLOROFORM-D
Creation_time     = 12-OCT-2008 00:15:52
Revision_time     = 10-DEC-2008 13:01:27
Current_time      = 10-DEC-2008 13:02:27

Comment           = Single Pulse Experime
Data_format       = 1D COMPLEX
Dim_size          = 16384
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 2.1823488[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 5[ppm]
X_points          = 16384
X_prescans        = 0
X_resolution      = 0.45822189[Hz]
X_sweep           = 7.50750751[kHz]
Clipped           = FALSE
Mod_return        = 1
Scans             = 8
Total_scans       = 8

X_90_width        = 10.5[us]
X_acq_time        = 2.1823488[s]
X_angle           = 45[deg]
X_pulse           = 9.25[us]
Initial_wait      = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 21
Relaxation_delay  = 4[s]
Temp_get          = 25.8[dC]
Unblank_time      = 2[us]
```


78

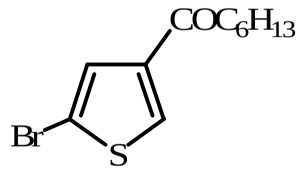


Filename = 5-Br-Hept-Th-3.jdf
Author = delta
Experiment = single_pulse.exp
Sample_id = S#604200
Solvent = CHLOROFORM-D
Creation_time = 12-OCT-2008 00:15:52
Revision_time = 10-DEC-2008 13:02:56
Current_time = 10-DEC-2008 13:03:06

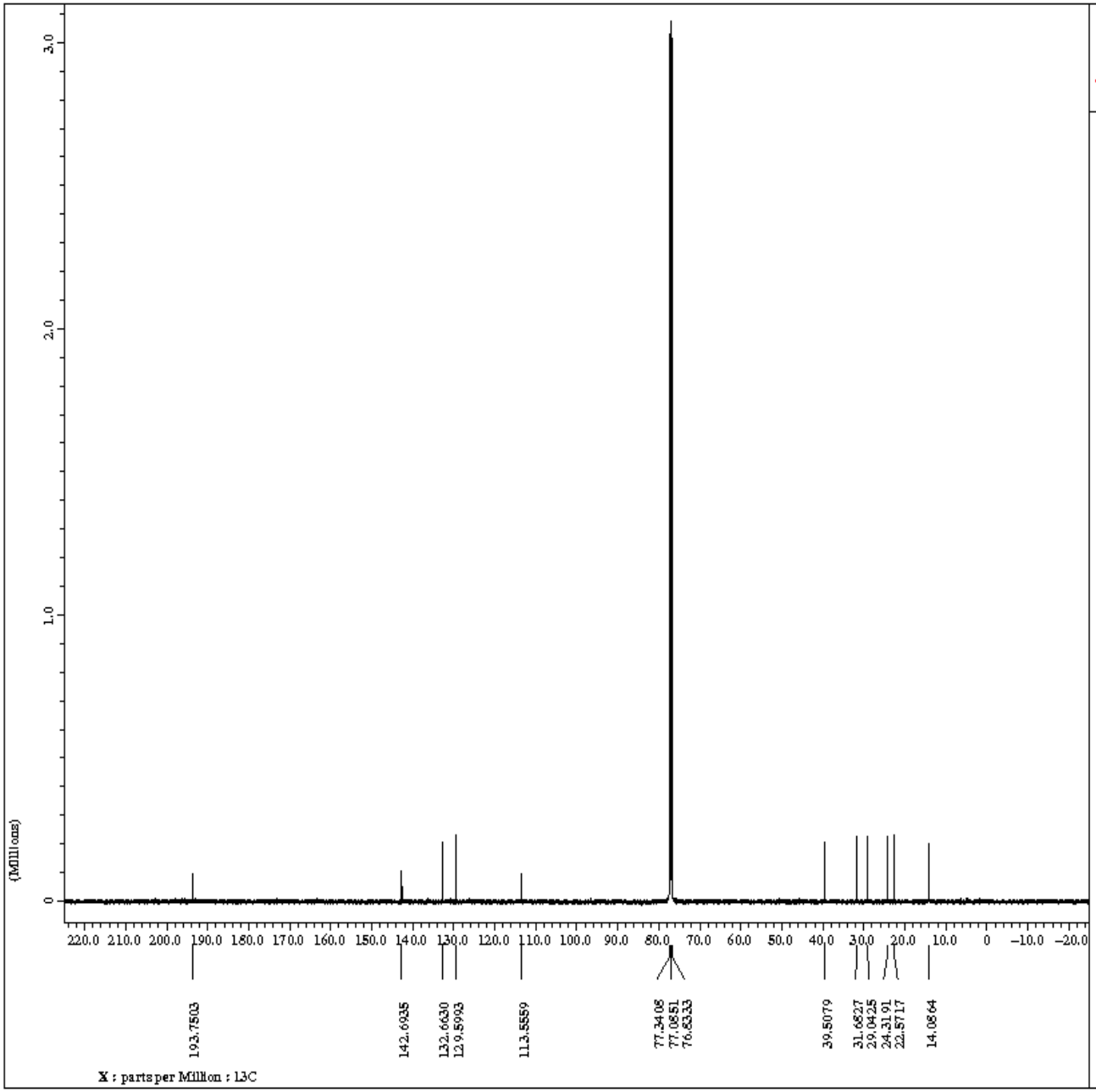
Comment = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR

Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8

X_90_width = 18.5[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 21
Relaxation_delay = 4[s]
Temp_get = 25.8[dC]
Unblank_time = 2[us]

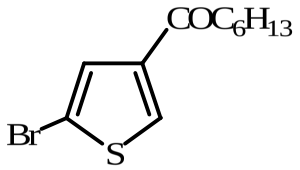


78

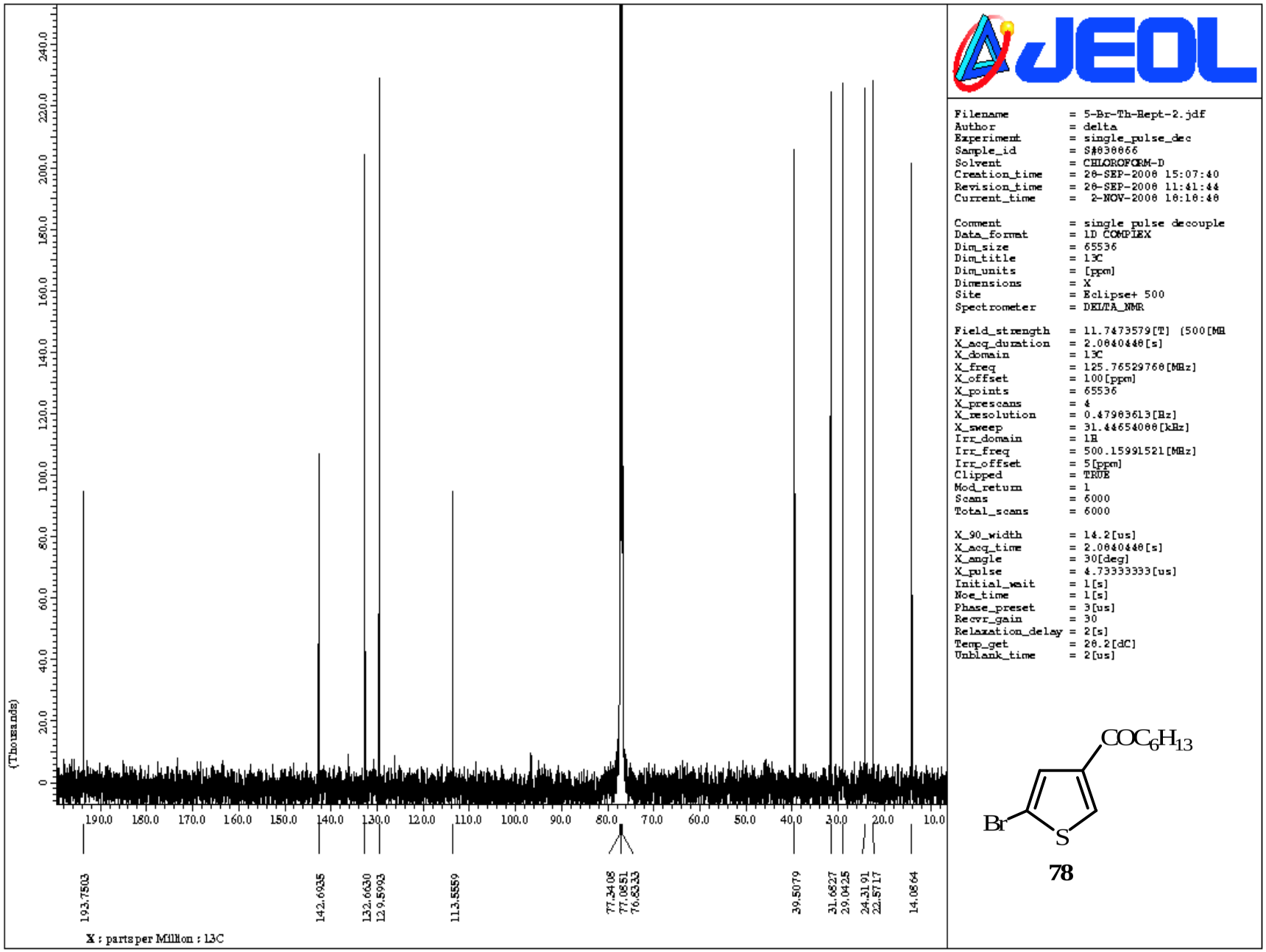


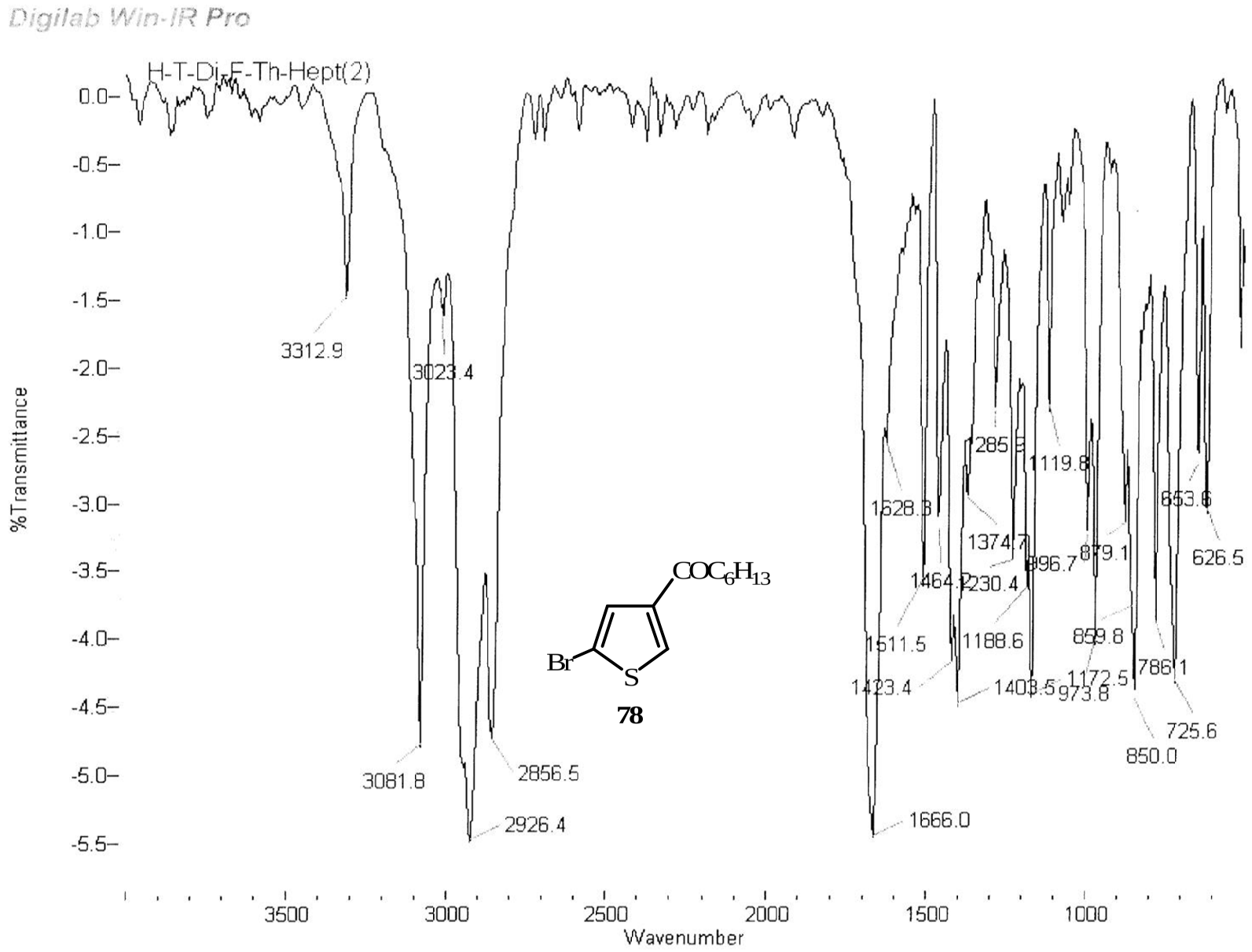
JEOL

Filename	= 5-Br-Th-Hept-2.jdf
Author	= delta
Experiment	= single_pulse_dec
Sample_id	= S#030866
Solvent	= CHLOROFORM-D
Creation_time	= 28-SEP-2008 15:07:40
Revision_time	= 28-SEP-2008 11:41:44
Current_time	= 2-NOV-2008 10:16:56
Comment	= single pulse decouple
Data_format	= 1D COMPLEX
Dim_size	= 65536
Dim_title	= 13C
Dim_units	= [ppm]
Dimensions	= X
Site	= Eclipse+ 500
Spectrometer	= DELTA_NMR
Field_strength	= 11.7473579[T] (500[MH
X_acq_duration	= 2.0840448[s]
X_domain	= 13C
X_freq	= 125.76529768[MHz]
X_offset	= 100[ppm]
X_points	= 65536
X_prescans	= 4
X_resolution	= 0.47983613[Hz]
X_sweep	= 31.44654088[kHz]
Irr_domain	= 1H
Irr_freq	= 500.15991521[MHz]
Irr_offset	= 5[ppm]
Clipped	= TRUE
Mod_return	= 1
Scans	= 6000
Total_scans	= 6000
X_90_width	= 14.2[us]
X_acq_time	= 2.0840448[s]
X_angle	= 30[deg]
X_pulse	= 4.73333333[us]
Initial_wait	= 1[s]
Noe_time	= 1[s]
Phase_preset	= 3[us]
Recvr_gain	= 30
Relaxation_delay	= 2[s]
Temp_get	= 28.2[dC]
Unblank_time	= 2[us]

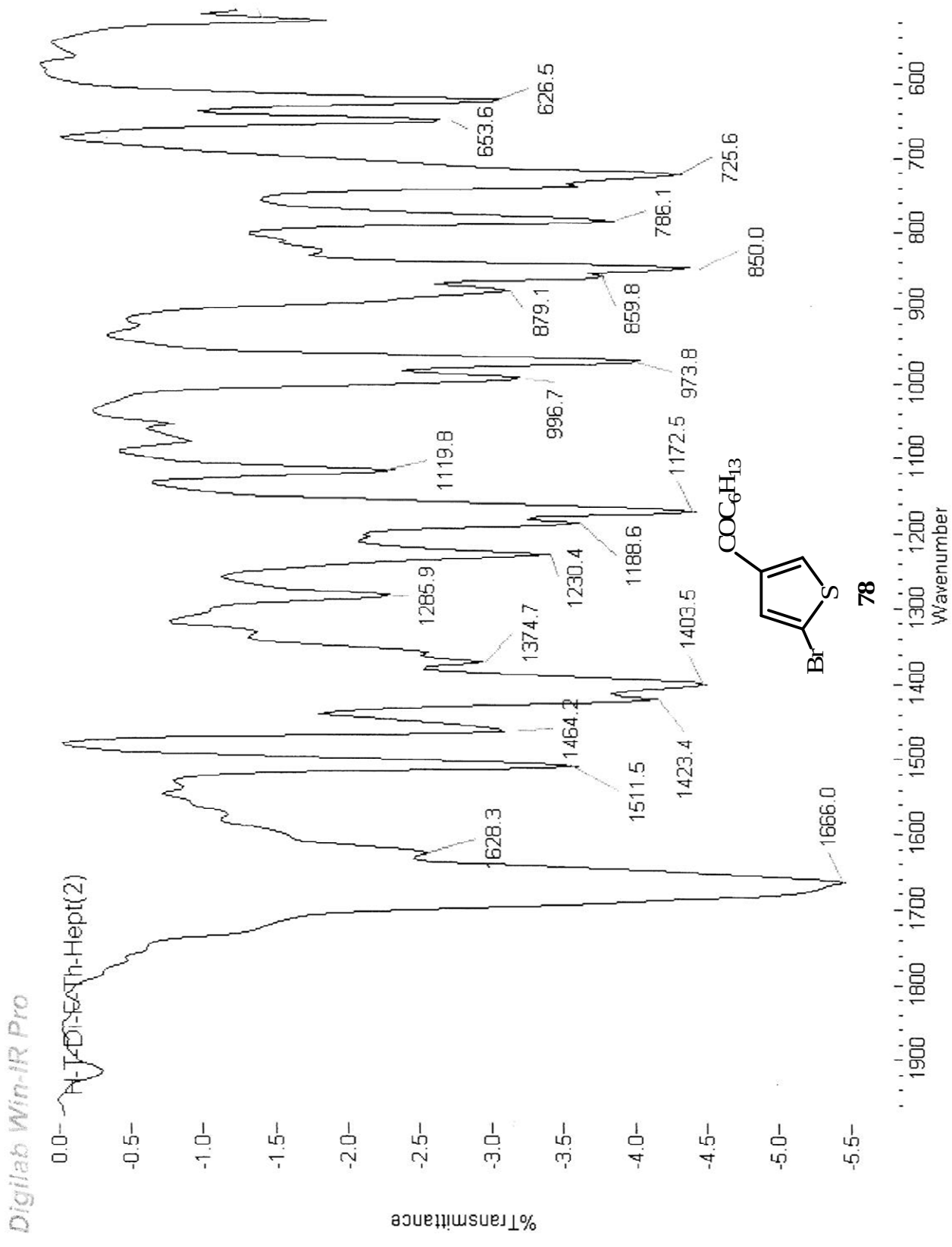


78


(Thousands)
240.0
220.0
200.0
180.0
160.0
140.0
120.0
100.0
80.0
60.0
40.0
20.0
0
190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0
193.7503
142.6935
132.6630
129.5993
113.5559
77.3408
77.0851
76.8333
39.5079
31.6827
29.0425
24.3191
22.8717
14.0864
X : parts per Million : 13C
JEOL
Filename = 5-Br-Th-Hept-2.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = S#030866
Solvent = CHLOROFORM-D
Creation_time = 28-SEP-2006 15:07:40
Revision_time = 28-SEP-2006 11:41:44
Current_time = 2-NOV-2006 10:10:48
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 65536
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.0840448[s]
X_domain = 13C
X_freq = 125.76529768[MHz]
X_offset = 100[ppm]
X_points = 65536
X_prescans = 4
X_resolution = 0.47983613[Hz]
X_sweep = 31.44654088[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5[ppm]
Clipped = TRUE
Mod_return = 1
Scans = 6000
Total_scans = 6000
X_90_width = 14.2[us]
X_acq_time = 2.0840448[s]
X_angle = 30[deg]
X_pulse = 4.73333333[us]
Initial_wait = 1[s]
Noe_time = 1[s]
Phase_preset = 3[us]
Recvr_gain = 30
Relaxation_delay = 2[s]
Temp_get = 28.2[dC]
Unblank_time = 2[us]
COC6H13
Br
S
78


Digilab Win-IR Pro
H-T-Di-F-Th-Hept(2)
%Transmittance
Wavenumber
3312.9
3023.4
3081.8
2856.5
2926.4
1666.0
1628.3
1511.5
1464.2
1423.4
1374.7
1403.5
1230.4
1188.6
1119.8
1172.5
973.8
896.7
879.1
859.8
786.1
725.6
850.0
653.6
626.5
Br
S
COC6H13

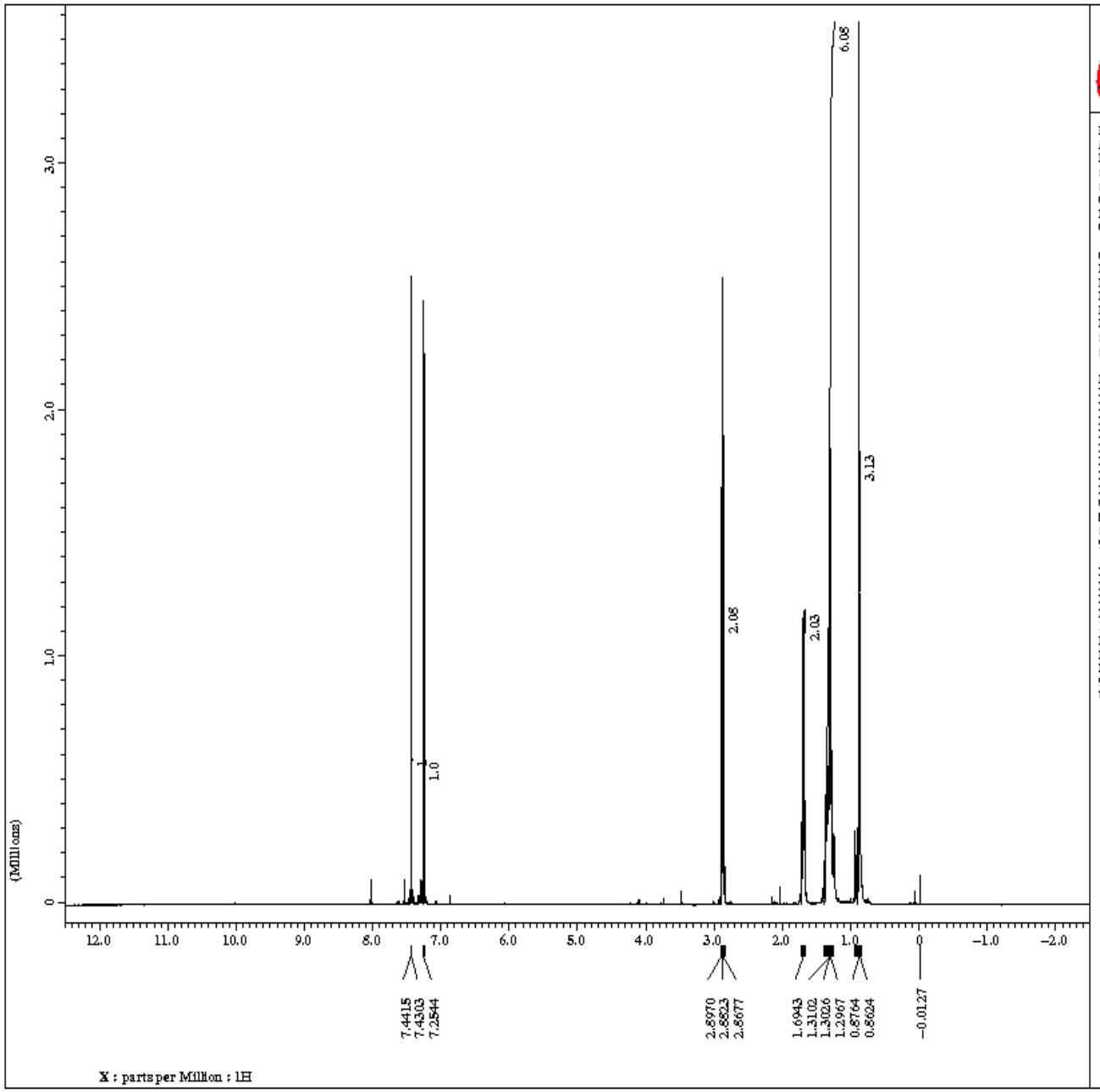
78


Digilab Win-IR Pro
%Transmittance
Wavenumber
626.5
653.6
725.6
786.1
850.0
879.1
859.8
973.8
996.7
1119.8
1172.5
1188.6
1230.4
1285.9
1374.7
1403.5
1423.4
1464.2
1511.5
1628.3
1666.0
COC6H13
Br
S

78

APPENDIX 7

^{1}H, ^{13}C NMR and IR spectra of 2-iodo-3-heptanoylthiophene (**81**)

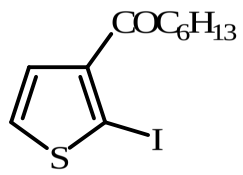


Filename = 2-I-Hept-Th-6.jdf
Author = delta
Experiment = single_pulse.exp
Sample_id = S#740950
Solvent = CHLOROFORM-D
Creation_time = 9-MAY-2007 00:06:20
Revision_time = 8-MAY-2007 21:00:38
Current_time = 3-NOV-2008 10:59:17

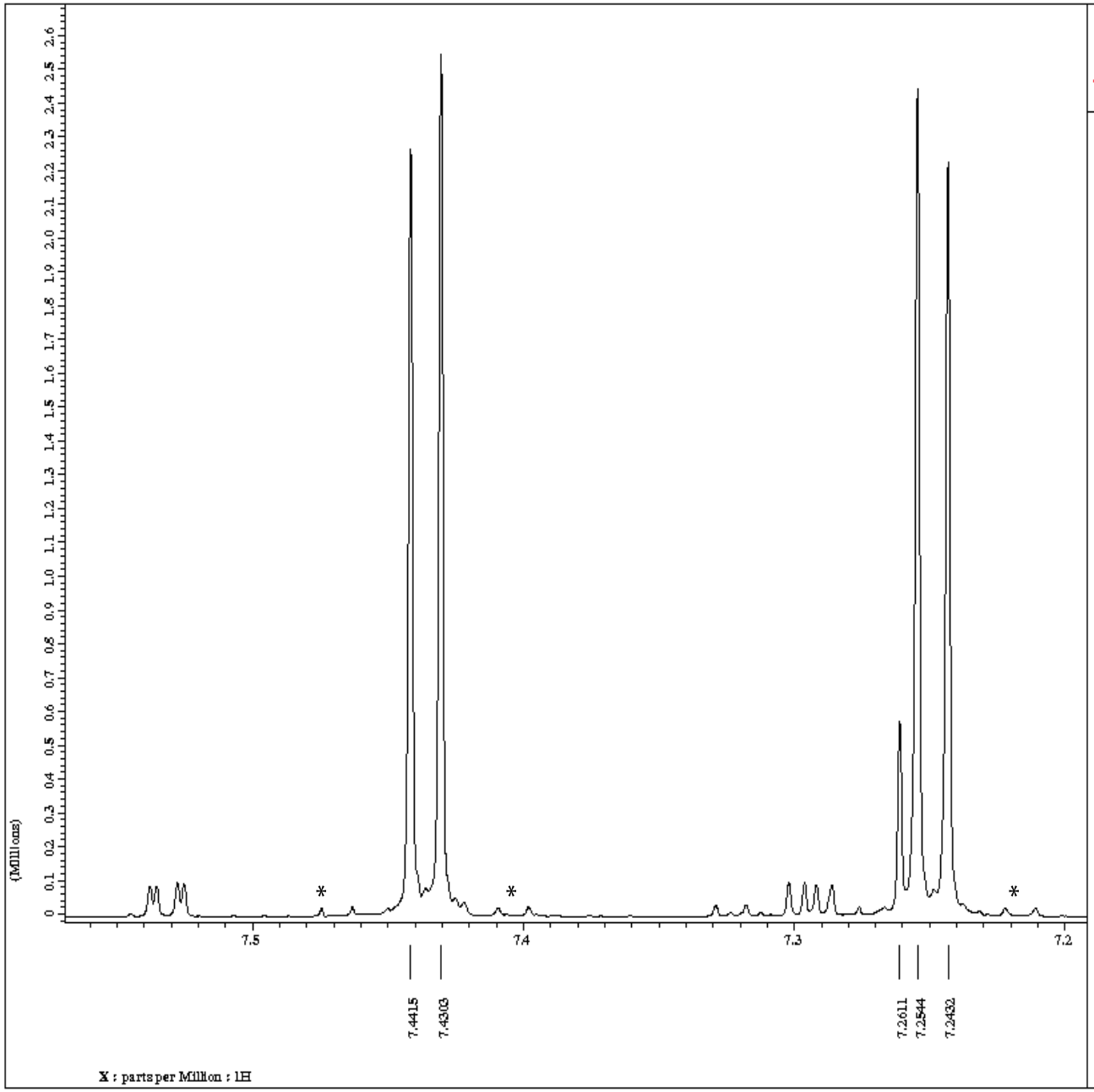
Comment = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 65536
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR

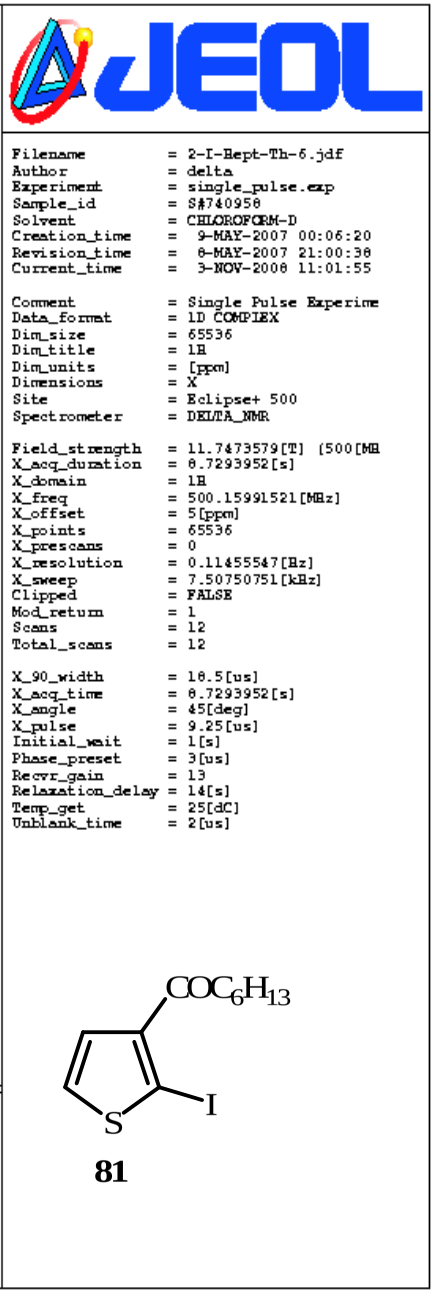
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 0.7293952[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 65536
X_prescans = 0
X_resolution = 0.11455547[Hz]
X_sweep = 7.50750751[kHz]
Clipped = FALSE
Mod_return = 1
Scans = 12
Total_scans = 12

X_90_width = 18.5[us]
X_acq_time = 0.7293952[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 13
Relaxation_delay = 14[s]
Temp_get = 25[dC]
Unblank_time = 2[us]

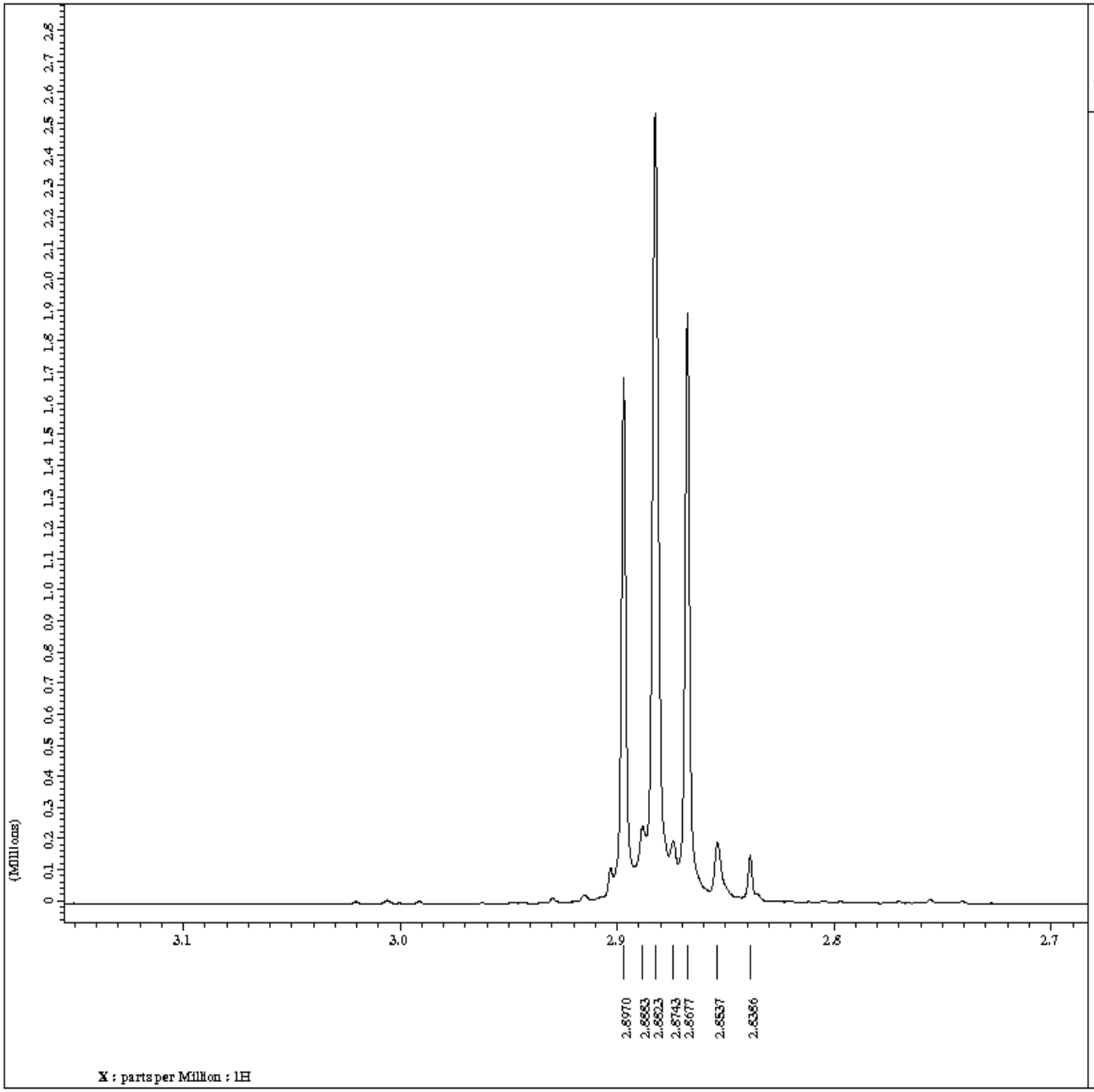


81


(Millions)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
2.0
2.1
2.2
2.3
2.4
2.5
2.6
7.5
7.4
7.3
7.2
*
*
*
7.4415
7.4303
7.2611
7.2544
7.2432
X : parts per Million : 1H


JEOL
Filename = 2-I-Hept-Th-6.jdf
Author = delta
Experiment = single_pulse.exp
Sample_id = S#740950
Solvent = CHLOROFORM-D
Creation_time = 9-MAY-2007 00:06:20
Revision_time = 8-MAY-2007 21:00:30
Current_time = 3-NOV-2008 11:01:55
Comment = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 65536
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 0.7293952[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 65536
X_prescans = 0
X_resolution = 0.11455547[Hz]
X_sweep = 7.50750751[kHz]
Clipped = FALSE
Mod_return = 1
Scans = 12
Total_scans = 12
X_90_width = 10.5[us]
X_acq_time = 0.7293952[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 13
Relaxation_delay = 14[s]
Temp_get = 25[dC]
Unblank_time = 2[us]
COC6H13
S
I

81



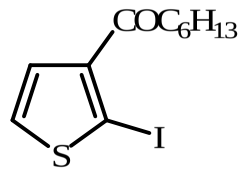
JEOL

Filename = 2-I-Hept-Th-6.jdf
Author = delta
Experiment = single_pulse.exp
Sample_id = S#740950
Solvent = CHLOROFORM-D
Creation_time = 9-MAY-2007 00:06:20
Revision_time = 8-MAY-2007 21:00:38
Current_time = 3-NOV-2008 11:05:18

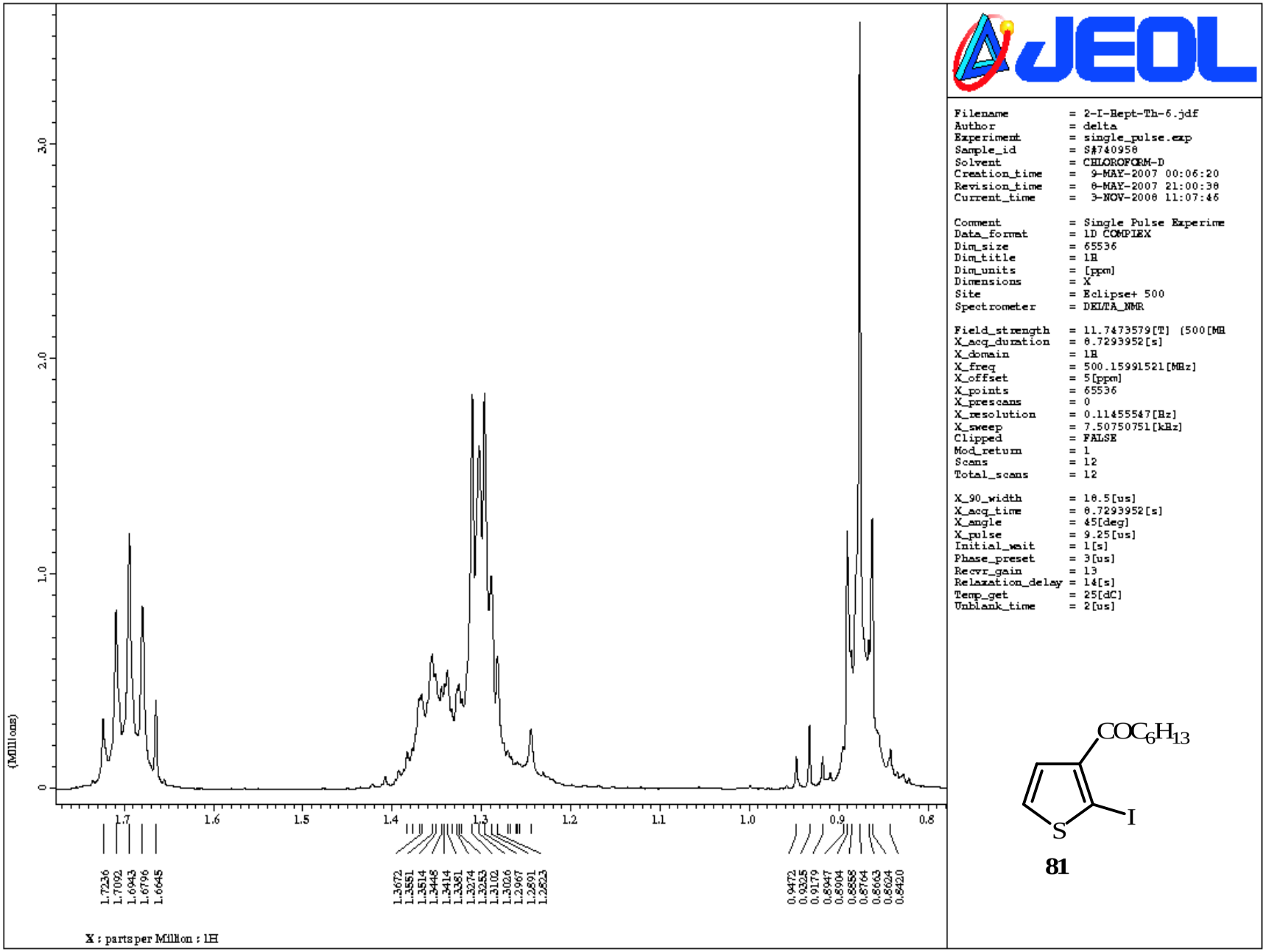
Comment = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 65536
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR

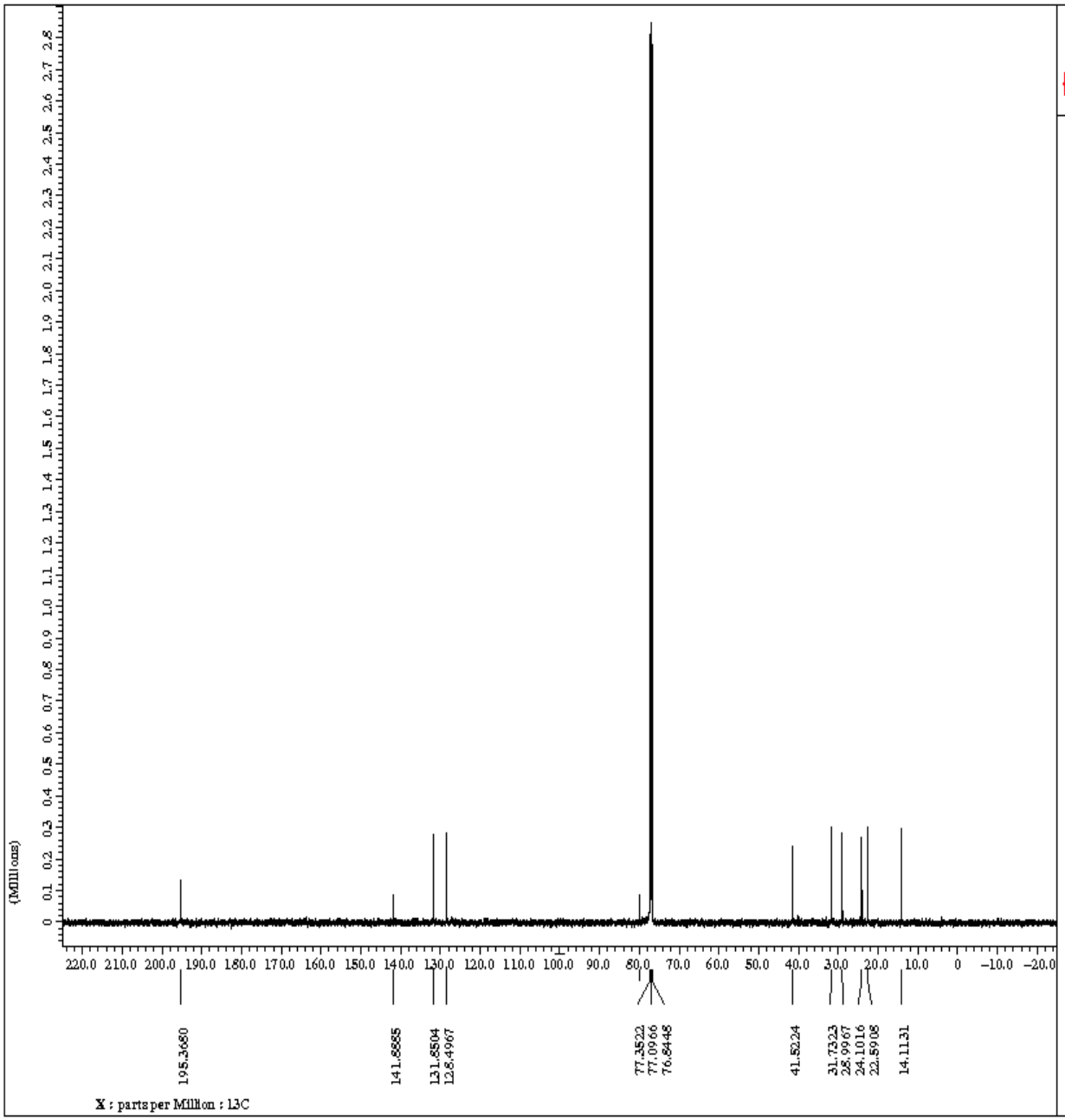
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 0.7293952[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 65536
X_prescans = 0
X_resolution = 0.11455547[Hz]
X_sweep = 7.50750751[kHz]
Clipped = FALSE
Mod_return = 1
Scans = 12
Total_scans = 12

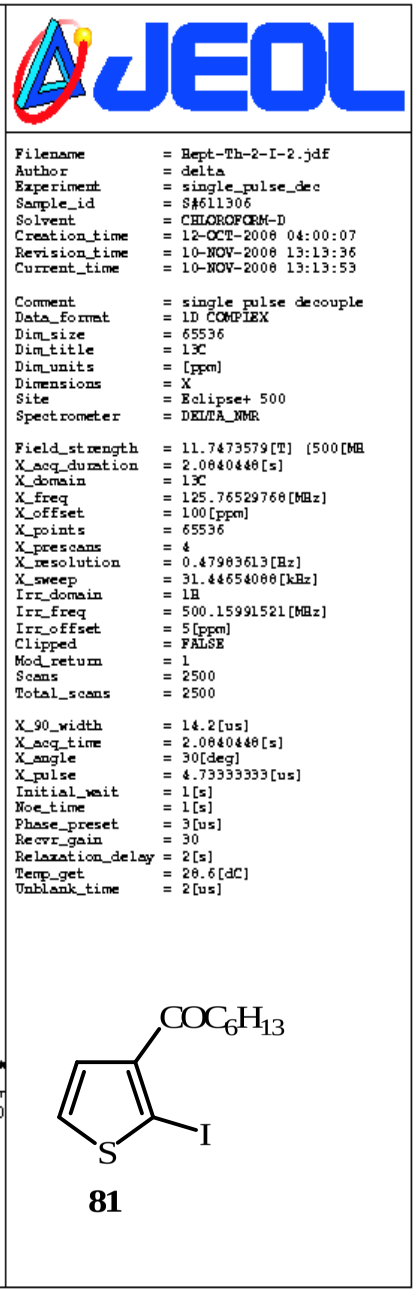
X_90_width = 18.5[us]
X_acq_time = 0.7293952[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 13
Relaxation_delay = 14[s]
Temp_get = 25[dC]
Unblank_time = 2[us]



81


(Millions)
3.0
2.0
1.0
0
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
1.7236
1.7092
1.6943
1.6796
1.6645
1.3672
1.3551
1.3514
1.3448
1.3414
1.3381
1.3274
1.3253
1.3102
1.3026
1.2967
1.2891
1.2823
0.9472
0.9325
0.9179
0.8947
0.8904
0.8858
0.8764
0.8663
0.8624
0.8420
X : parts per Million : 1H
Filename = 2-I-Hept-Th-6.jdf
Author = delta
Experiment = single_pulse.exp
Sample_id = S#740958
Solvent = CHLOROFORM-D
Creation_time = 9-MAY-2007 00:06:20
Revision_time = 8-MAY-2007 21:00:38
Current_time = 3-NOV-2008 11:07:46
Comment = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 65536
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 0.7293952[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 65536
X_prescans = 0
X_resolution = 0.11455547[Hz]
X_sweep = 7.50750751[kHz]
Clipped = FALSE
Mod_return = 1
Scans = 12
Total_scans = 12
X_90_width = 10.5[us]
X_acq_time = 0.7293952[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 13
Relaxation_delay = 14[s]
Temp_get = 25[dC]
Unblank_time = 2[us]
COC6H13
S
I
81





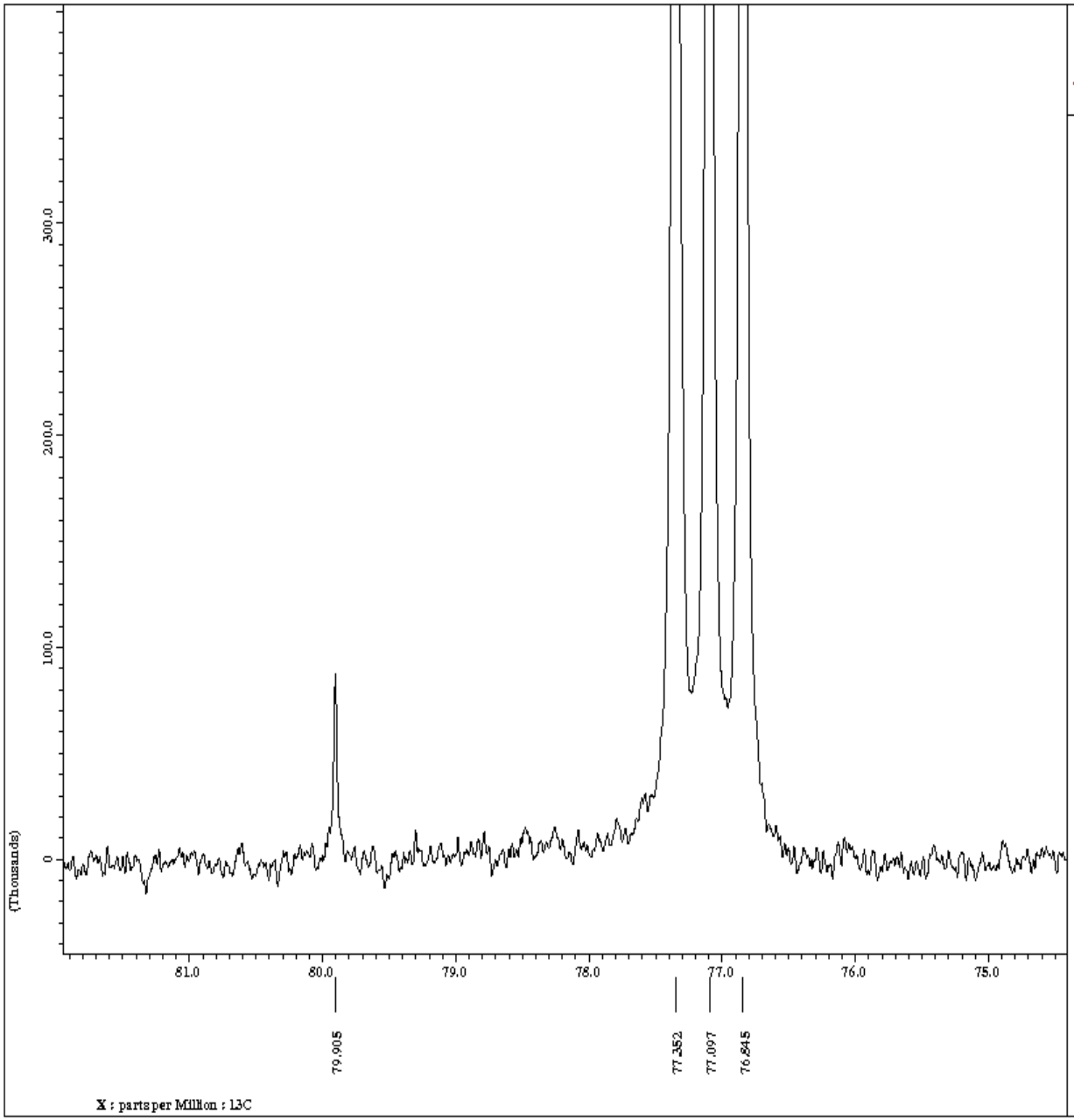

```
Filename          = Hept-Th-2-I-2.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#611306
Solvent           = CHLOROFORM-D
Creation_time     = 12-OCT-2008 04:00:07
Revision_time     = 10-NOV-2008 13:13:36
Current_time      = 10-NOV-2008 13:13:53

Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 65536
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 2.0840448[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 65536
X_prescans        = 4
X_resolution      = 0.47980613[Hz]
X_sweep           = 31.44654088[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 2500
Total_scans       = 2500

X_90_width        = 14.2[us]
X_acq_time        = 2.0840448[s]
X_angle           = 30[deg]
X_pulse           = 4.73333333[us]
Initial_wait      = 1[s]
Noe_time          = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 30
Relaxation_delay  = 2[s]
Temp_get          = 28.6[dC]
Unblank_time      = 2[us]
```


81



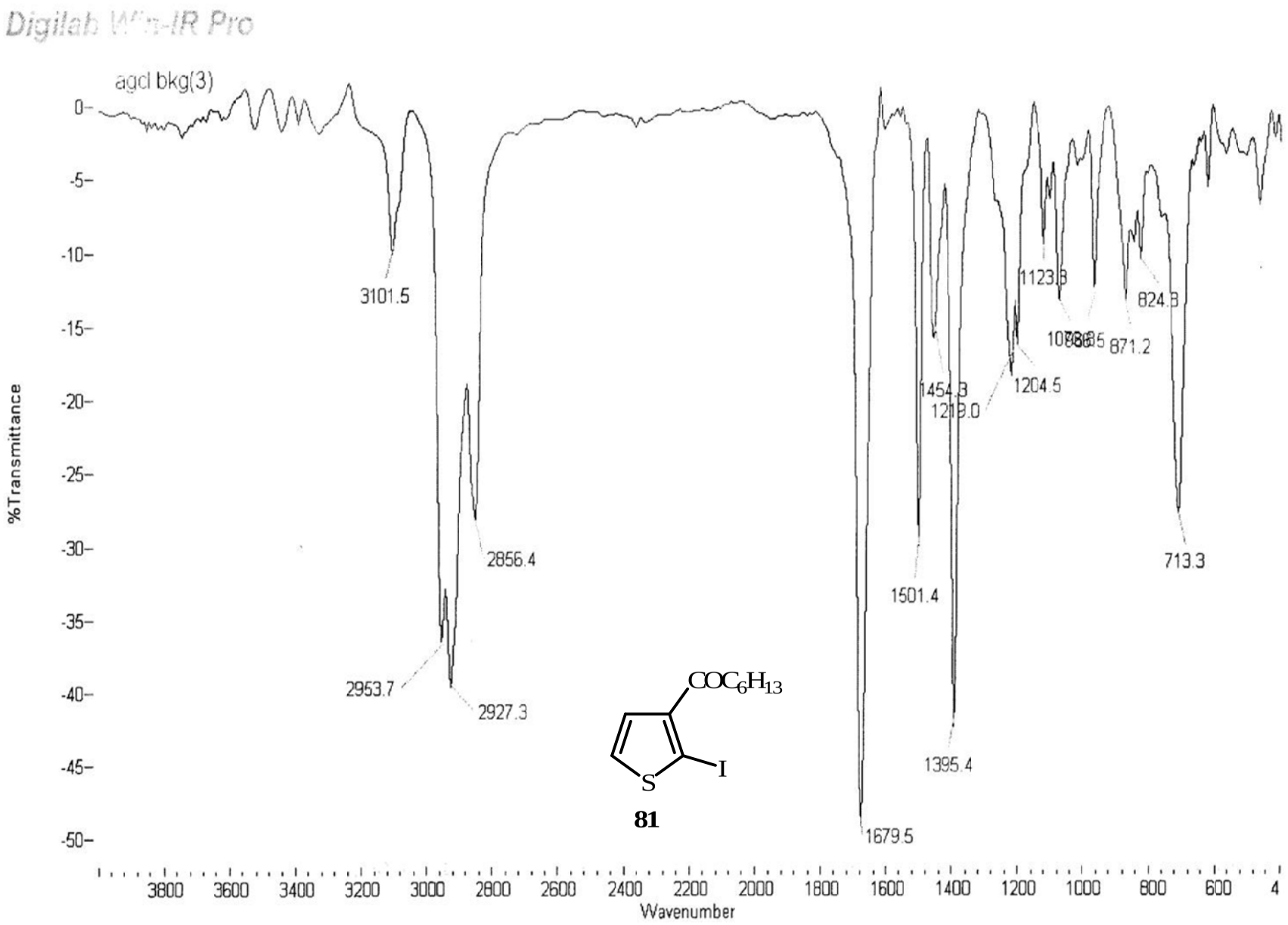
JEOL

```
Filename          = Rept-Th-2-I-2.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#611306
Solvent           = CHLOROFORM-D
Creation_time     = 12-OCT-2008 04:00:07
Revision_time     =  9-DEC-2008 07:01:12
Current_time      =  9-DEC-2008 07:04:31

Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 65536
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 2.0840448[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 65536
X_prescans        = 4
X_resolution      = 0.47983613[Hz]
X_sweep           = 31.44654088[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 2500
Total_scans       = 2500

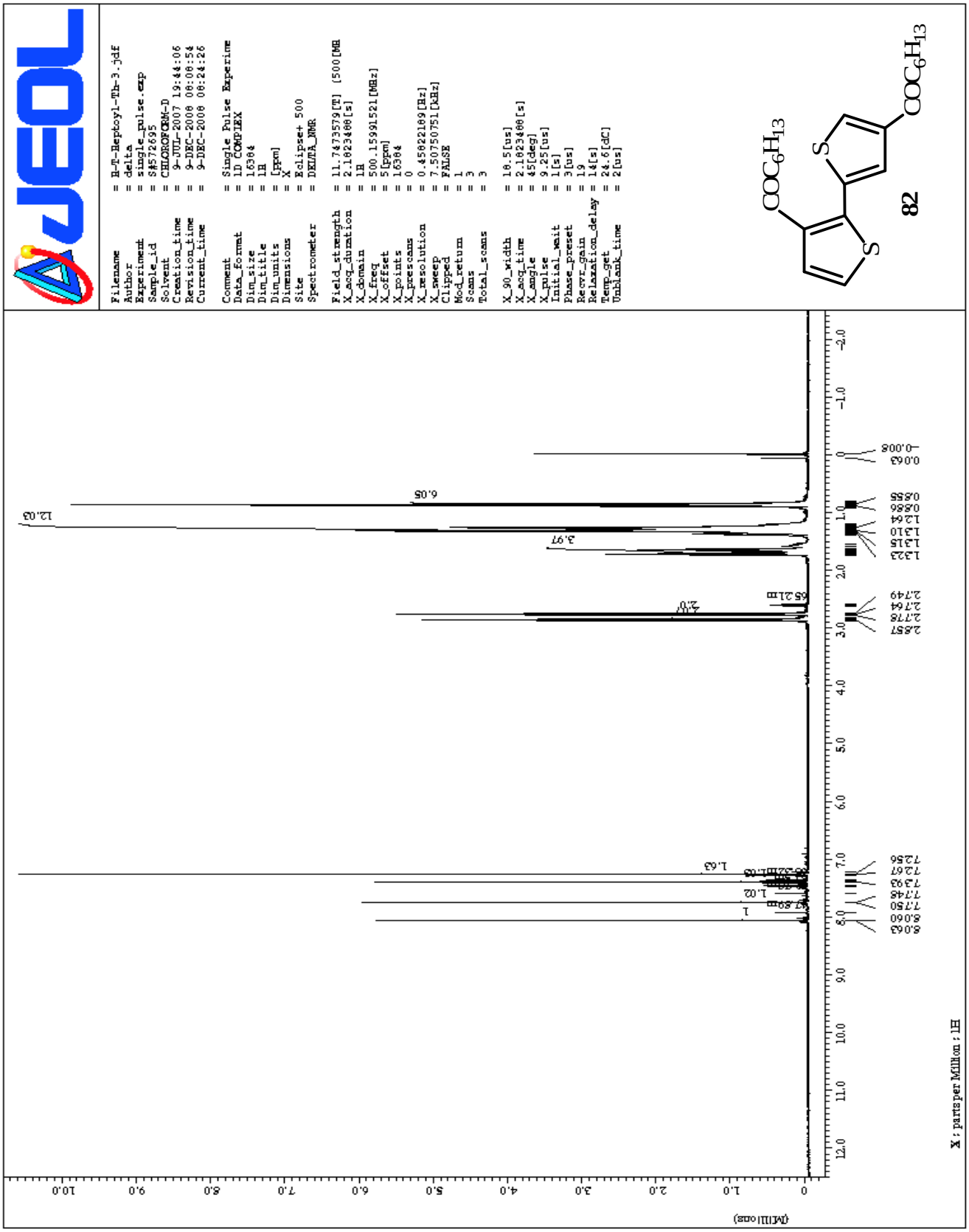
X_90_width        = 14.2[us]
X_acq_time        = 2.0840448[s]
X_angle           = 30[deg]
X_pulse           = 4.73333333[us]
Initial_wait      = 1[s]
Noe_time          = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 30
Relaxation_delay  = 2[s]
Temp_get          = 20.6[dC]
Unblank_time      = 2[us]
```

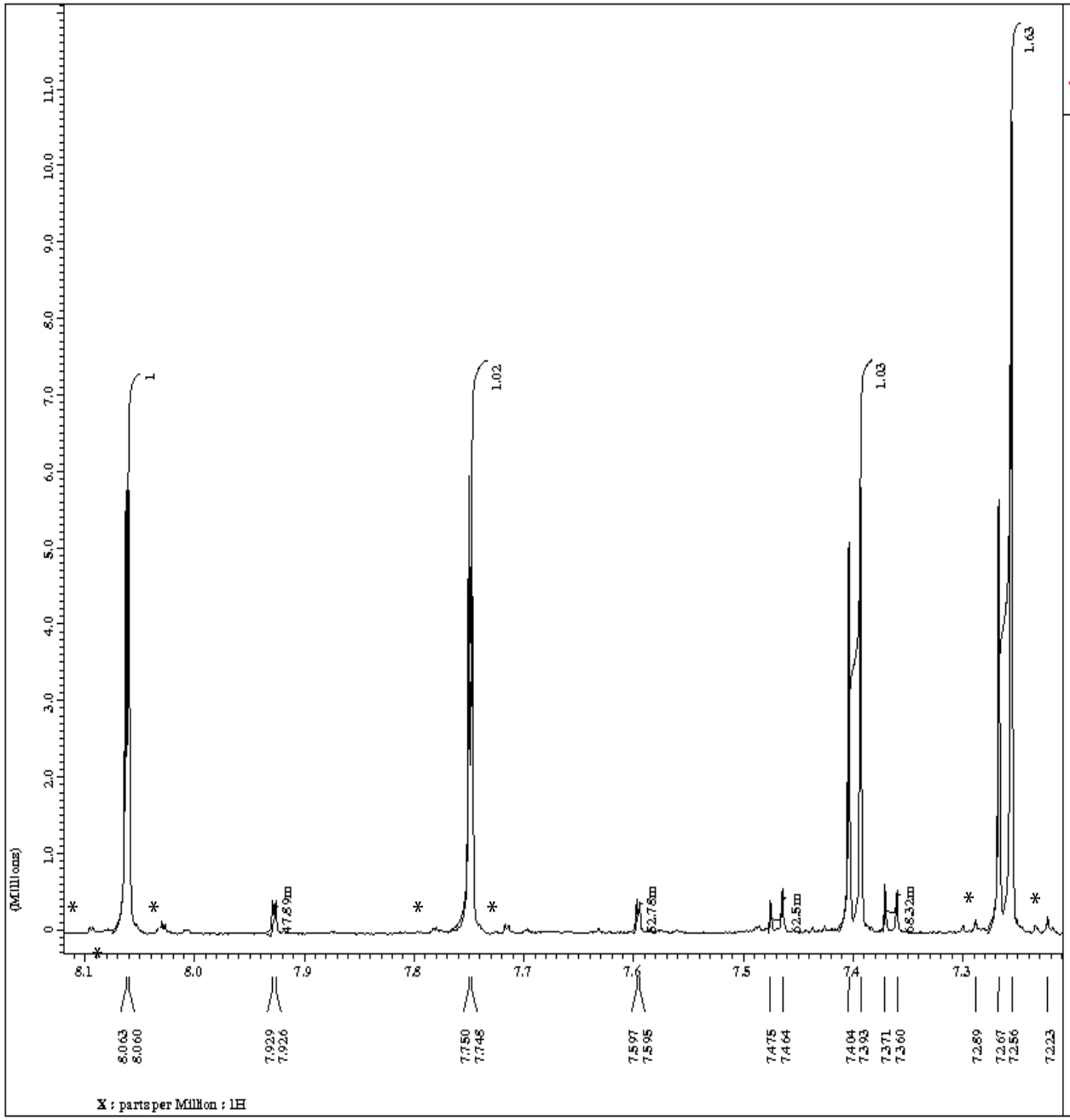

Digilab Win-IR Pro
agcl bkg(3)
%Transmittance
Wavenumber
3101.5
2953.7
2927.3
2856.4
1679.5
1501.4
1454.3
1395.4
1204.5
1123.3
871.2
824.3
713.3
COC_6H_{13}
I
S

81

APPENDIX 8

^{1}H ^{13}C NMR and IR spectra of 3,4'-diheptanoyl -2,2'-bithiophene (**82**)


JEOL
Filename = H-T-Heptoyl-Th-3.jdf
Author = delta
Experiment = single_pulse.exp
Sample_id = S#572695
Solvent = CHLOROFORM-D
Creation_time = 9-JUL-2007 19:44:06
Revision_time = 9-DEC-2008 06:06:54
Current_time = 9-DEC-2008 08:24:26
Comment = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823486[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822169[Hz]
X_sweep = 7.50750751[kHz]
Clipped = FALSE
Mod_return = 1
Scans = 3
Total_scans = 3
X_90_width = 10.5[us]
X_acq_time = 2.1823486[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 19
Relaxation_delay = 14[s]
Temp_get = 24.6[dC]
Unblank_time = 2[us]
COC6H13
S
S
COC6H13
82
12.03
6.05
3.97
2.00
1.63
1.02
1
8.063
8.060
7.750
7.748
7.393
7.267
7.256
2.857
2.778
2.764
2.749
1.323
1.315
1.310
1.264
0.886
0.855
0.063
-0.008
(Million)
X : parts per Million : 1H

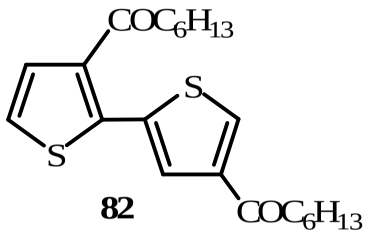


Filename = H-T-Heptoyl-Th-3.jdf
Author = delta
Experiment = single_pulse.exp
Sample_id = S#572695
Solvent = CHLOROFORM-D
Creation_time = 9-JUL-2007 19:44:06
Revision_time = 9-DEC-2008 08:24:47
Current_time = 9-DEC-2008 08:26:02

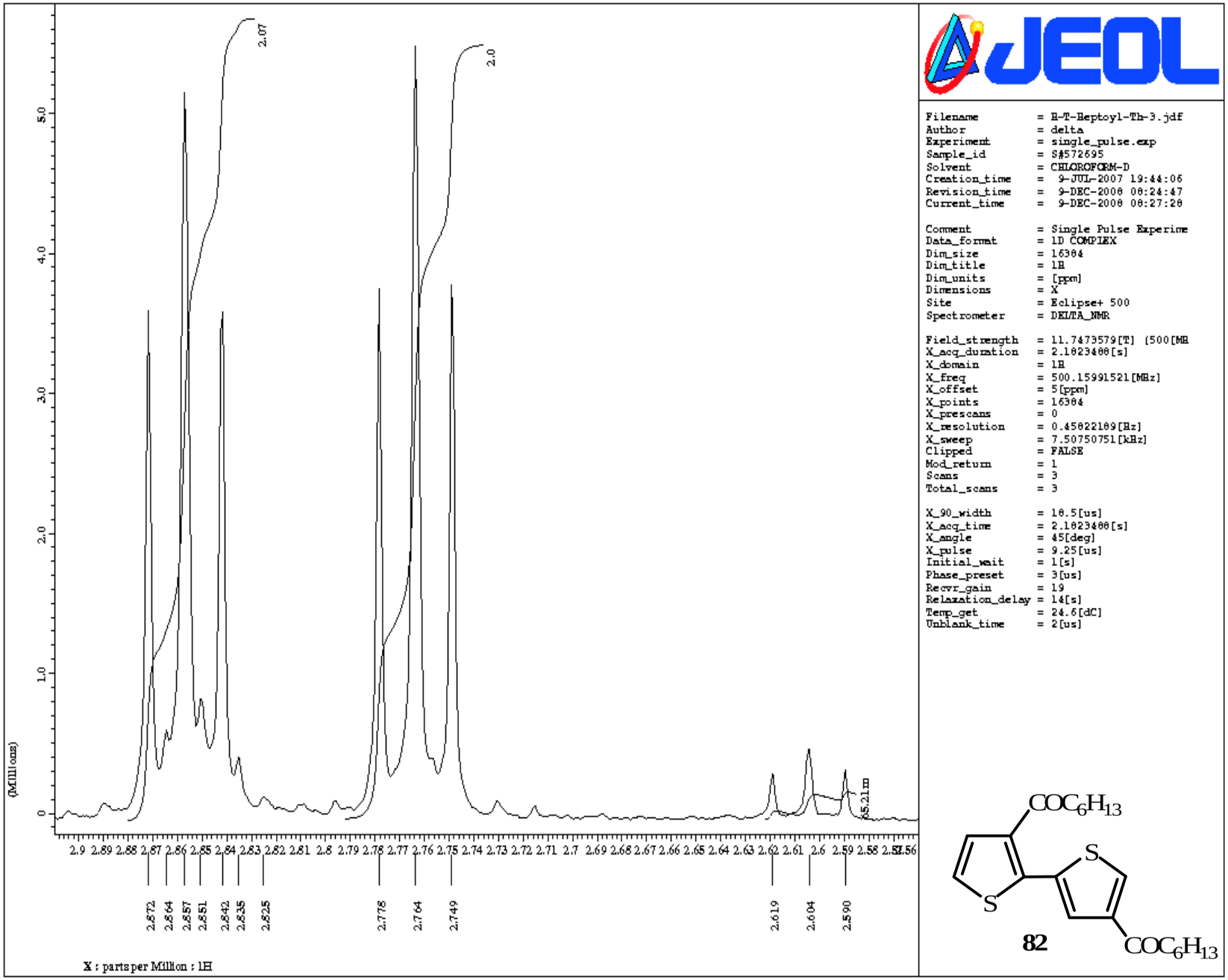
Comment = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR

Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Clipped = FALSE
Mod_return = 1
Scans = 3
Total_scans = 3

X_90_width = 18.5[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 19
Relaxation_delay = 14[s]
Temp_get = 24.6[dC]
Unblank_time = 2[us]



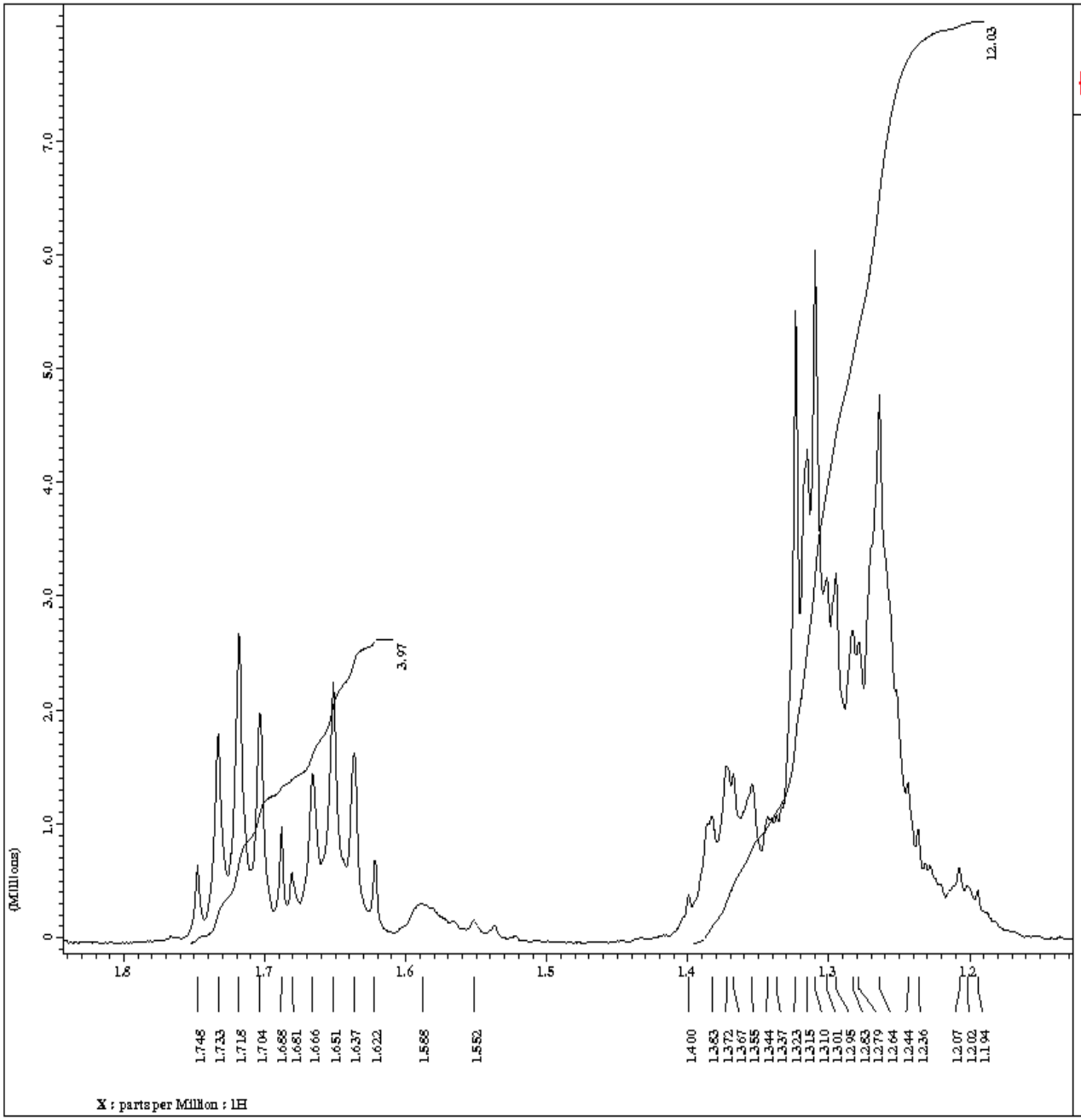
82



JEOL

Filename	= H-T-Heptoyl-Th-3.jdf
Author	= delta
Experiment	= single_pulse.exp
Sample_id	= S#572695
Solvent	= CHLOROFORM-D
Creation_time	= 9-JUL-2007 19:44:06
Revision_time	= 9-DEC-2008 08:24:47
Current_time	= 9-DEC-2008 08:27:28
Comment	= Single Pulse Experime
Data_format	= 1D COMPLEX
Dim_size	= 16384
Dim_title	= 1H
Dim_units	= [ppm]
Dimensions	= X
Site	= Eclipse+ 500
Spectrometer	= DELTA_NMR
Field_strength	= 11.7473579[T] (500[MH
X_acq_duration	= 2.1823488[s]
X_domain	= 1H
X_freq	= 500.15991521[MHz]
X_offset	= 5[ppm]
X_points	= 16384
X_prescans	= 0
X_resolution	= 0.45822189[Hz]
X_sweep	= 7.50750751[kHz]
Clipped	= FALSE
Mod_return	= 1
Scans	= 3
Total_scans	= 3
X_90_width	= 10.5[us]
X_acq_time	= 2.1823488[s]
X_angle	= 45[deg]
X_pulse	= 9.25[us]
Initial_wait	= 1[s]
Phase_preset	= 3[us]
Recvr_gain	= 19
Relaxation_delay	= 14[s]
Temp_get	= 24.6[dC]
Unblank_time	= 2[us]

82



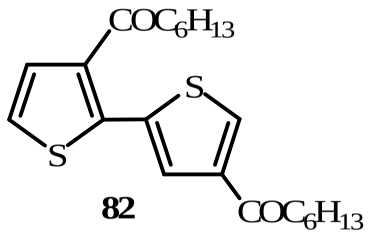
JEOL

```
Filename          = B-T-Heptoyl-Th-3.jdf
Author            = delta
Experiment        = single_pulse.exp
Sample_id         = S#572695
Solvent           = CHLOROFORM-D
Creation_time     =  9-JUL-2007 19:44:06
Revision_time     =  9-DEC-2008 08:24:47
Current_time      =  9-DEC-2008 08:27:57

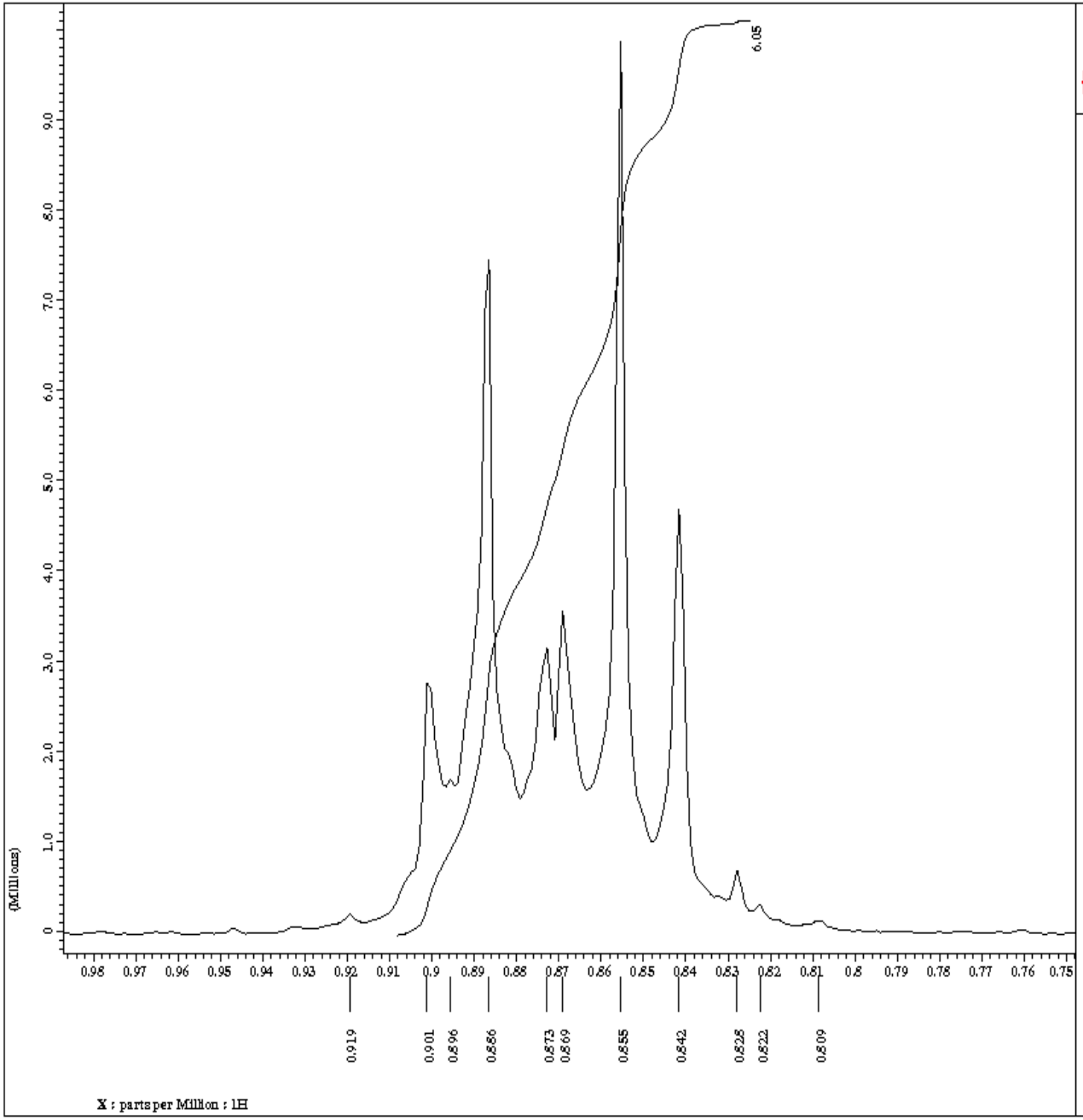
Comment           = Single Pulse Experime
Data_format       = 1D COMPLEX
Dim_size          = 16384
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 2.1023488[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 5[ppm]
X_points          = 16384
X_prescans        = 0
X_resolution      = 0.45822189[Hz]
X_sweep           = 7.50750751[kHz]
Clipped           = FALSE
Mod_return        = 1
Scans             = 3
Total_scans       = 3

X_90_width        = 10.5[us]
X_acq_time        = 2.1023488[s]
X_angle           = 45[deg]
X_pulse           = 9.25[us]
Initial_wait      = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 19
Relaxation_delay  = 14[s]
Temp_get          = 24.6[dC]
Unblank_time      = 2[us]
```



82



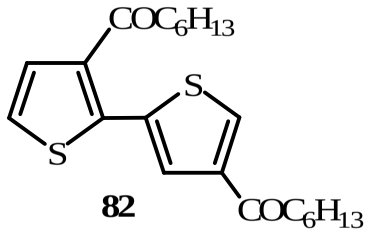
JEOL

```
Filename          = H-T-Heptoyl-Th-3.jdf
Author            = delta
Experiment        = single_pulse.exp
Sample_id         = S#572695
Solvent           = CHLOROFORM-D
Creation_time     =  9-JUL-2007 19:44:06
Revision_time     =  9-DEC-2008 08:24:47
Current_time      =  9-DEC-2008 08:28:30

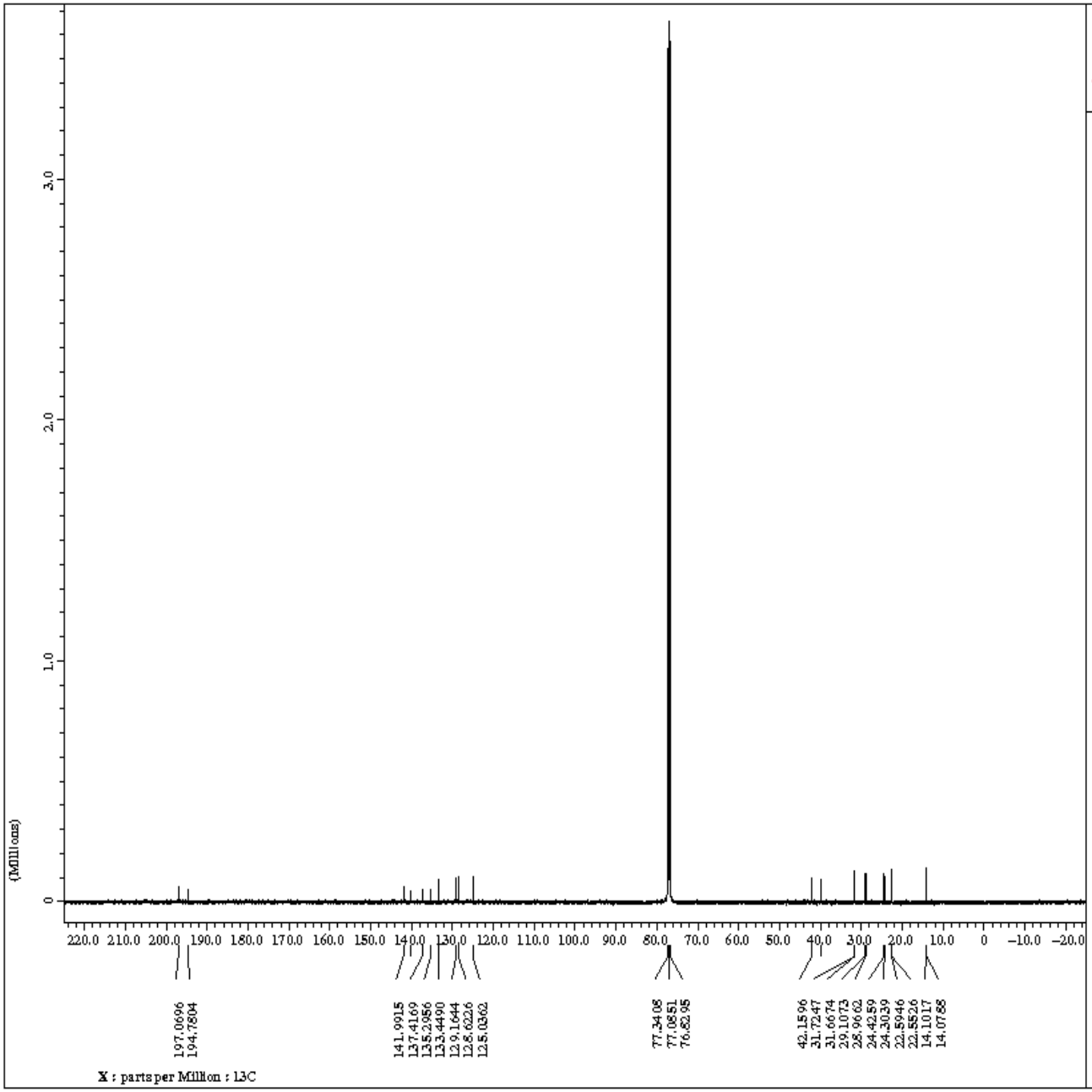
Comment           = Single Pulse Experime
Data_format       = 1D COMPLEX
Dim_size          = 16384
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 2.1823488[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 5[ppm]
X_points          = 16384
X_prescans        = 0
X_resolution      = 0.45822189[Hz]
X_sweep           = 7.50750751[kHz]
Clipped           = FALSE
Mod_return        = 1
Scans             = 3
Total_scans       = 3

X_90_width        = 10.5[us]
X_acq_time        = 2.1823488[s]
X_angle           = 45[deg]
X_pulse           = 9.25[us]
Initial_wait      = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 19
Relaxation_delay  = 14[s]
Temp_get          = 24.6[dC]
Unblank_time      = 2[us]
```



82



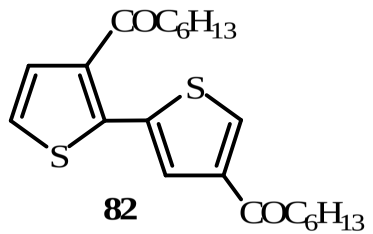
JEOL

Filename = H-T-Hex-Th-3.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = S#845796
Solvent = CHLOROFORM-D
Creation_time = 13-NOV-2008 17:08:49
Revision_time = 13-NOV-2008 12:31:01
Current_time = 13-NOV-2008 12:33:32

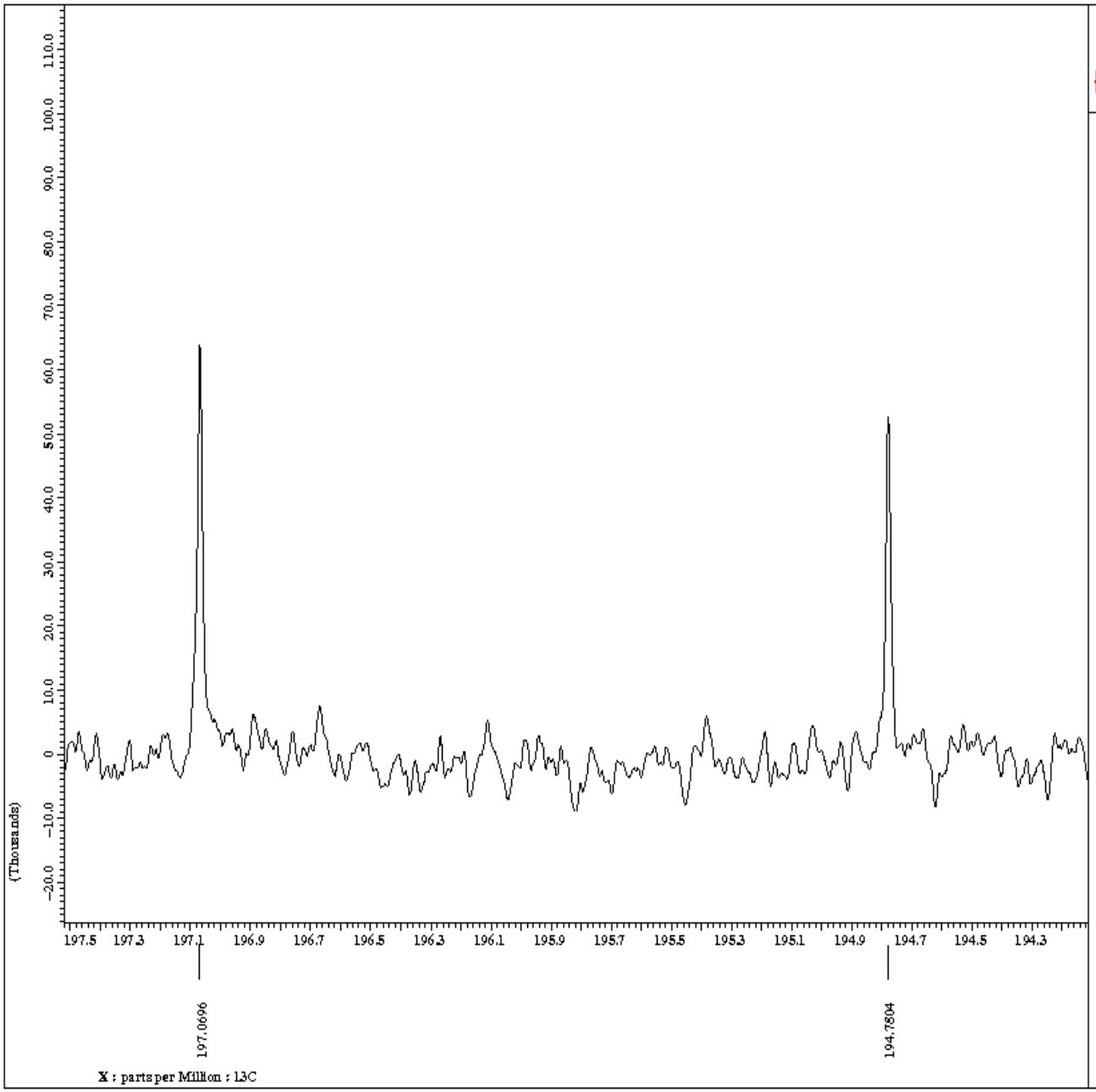
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 65536
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR

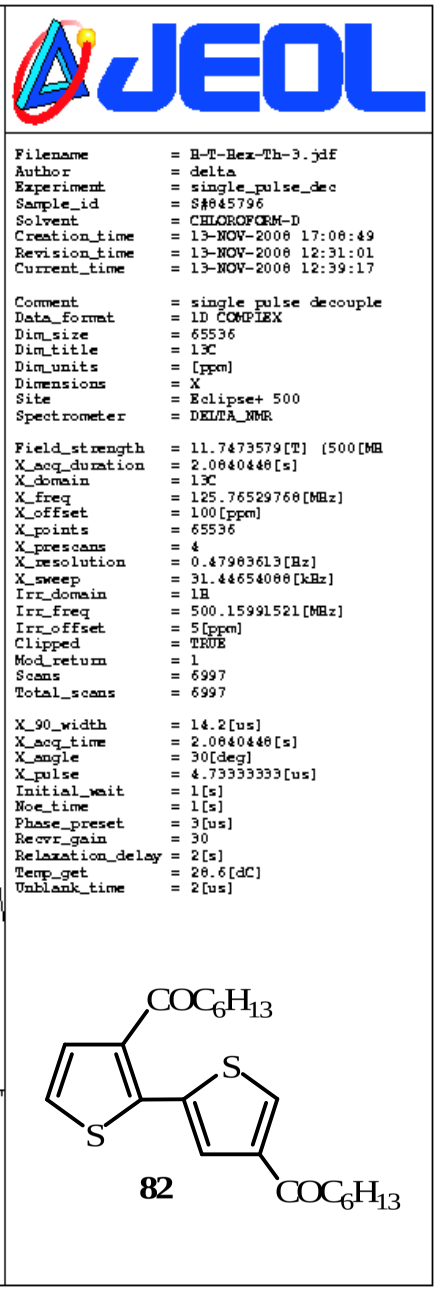
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.0840448[s]
X_domain = 13C
X_freq = 125.76529768[MHz]
X_offset = 100[ppm]
X_points = 65536
X_prescans = 4
X_resolution = 0.47983613[Hz]
X_sweep = 31.44654088[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5[ppm]
Clipped = TRUE
Mod_return = 1
Scans = 6997
Total_scans = 6997

X_90_width = 14.2[us]
X_acq_time = 2.0840448[s]
X_angle = 30[deg]
X_pulse = 4.73333333[us]
Initial_wait = 1[s]
Noe_time = 1[s]
Phase_preset = 3[us]
Recvr_gain = 30
Relaxation_delay = 2[s]
Temp_get = 28.6[dC]
Unblank_time = 2[us]



82





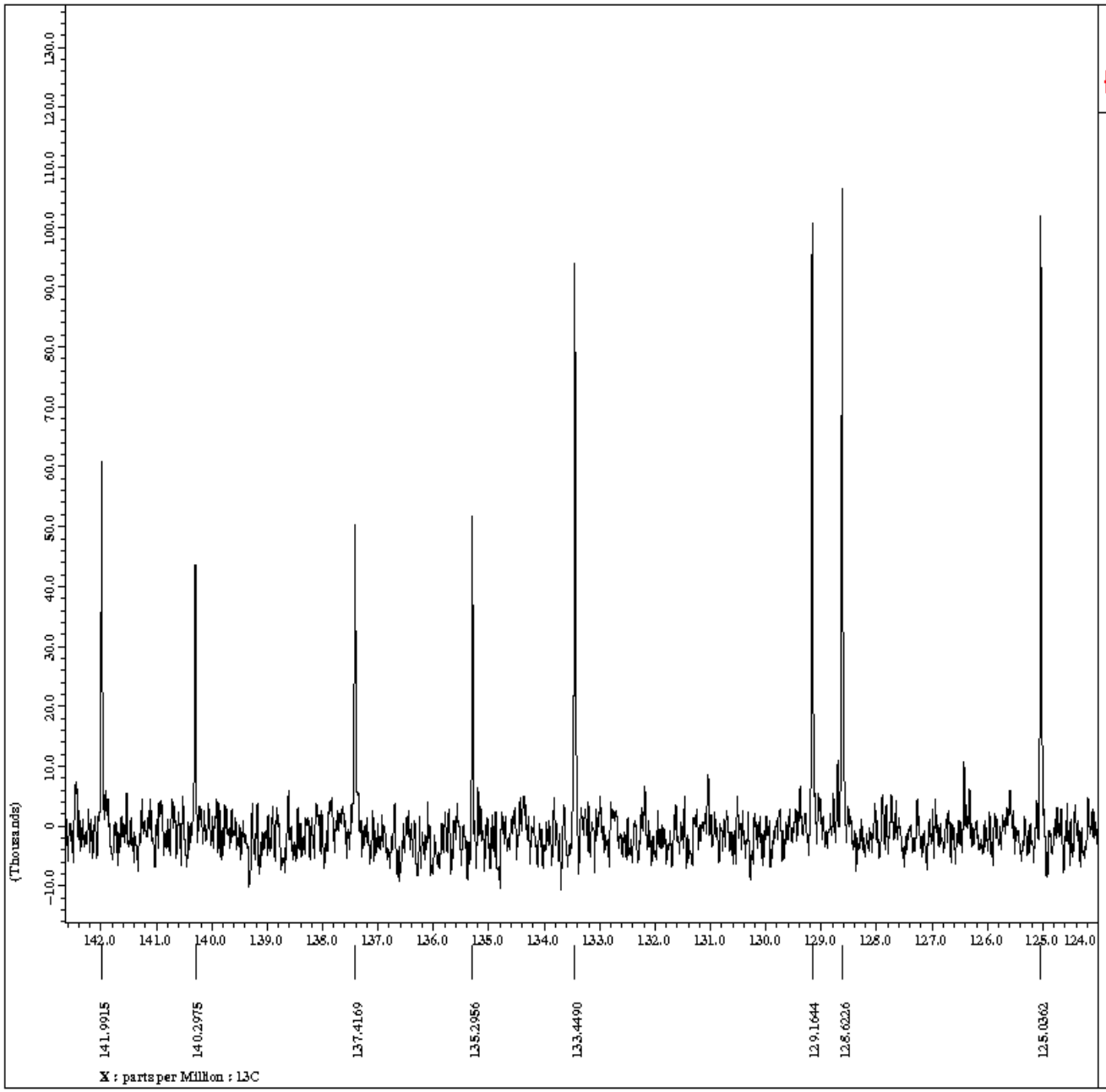

```
Filename          = H-T-Hex-Th-3.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#045796
Solvent           = CHLOROFORM-D
Creation_time     = 13-NOV-2008 17:08:49
Revision_time     = 13-NOV-2008 12:31:01
Current_time      = 13-NOV-2008 12:39:17

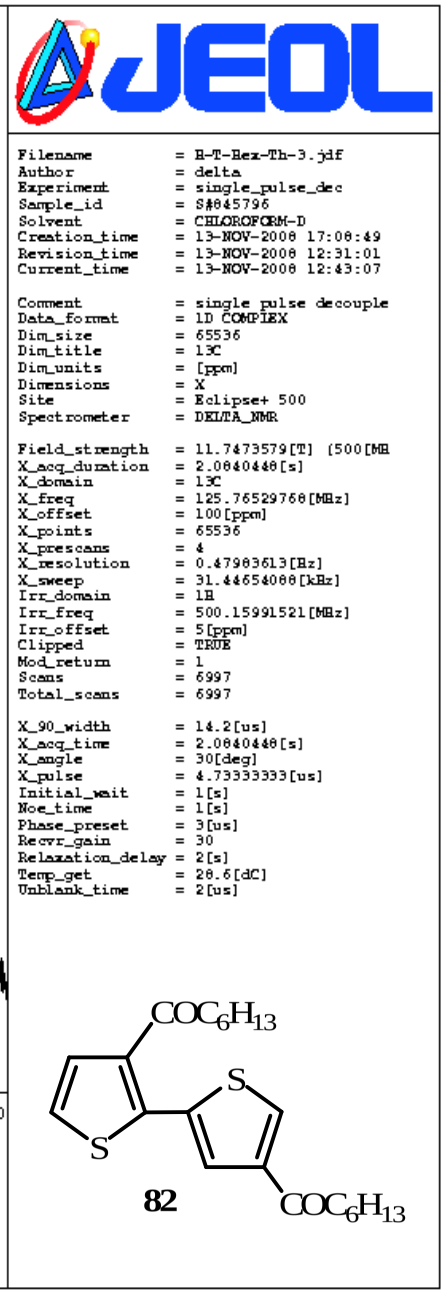
Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 65536
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 2.0840448[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 65536
X_prescans        = 4
X_resolution      = 0.47983613[Hz]
X_sweep           = 31.44654088[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5[ppm]
Clipped           = TRUE
Mod_return        = 1
Scans             = 6997
Total_scans       = 6997

X_90_width        = 14.2[us]
X_acq_time        = 2.0840448[s]
X_angle           = 30[deg]
X_pulse           = 4.73333333[us]
Initial_wait      = 1[s]
Noe_time          = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 30
Relaxation_delay  = 2[s]
Temp_get          = 28.6[dC]
Unblank_time      = 2[us]
```


82





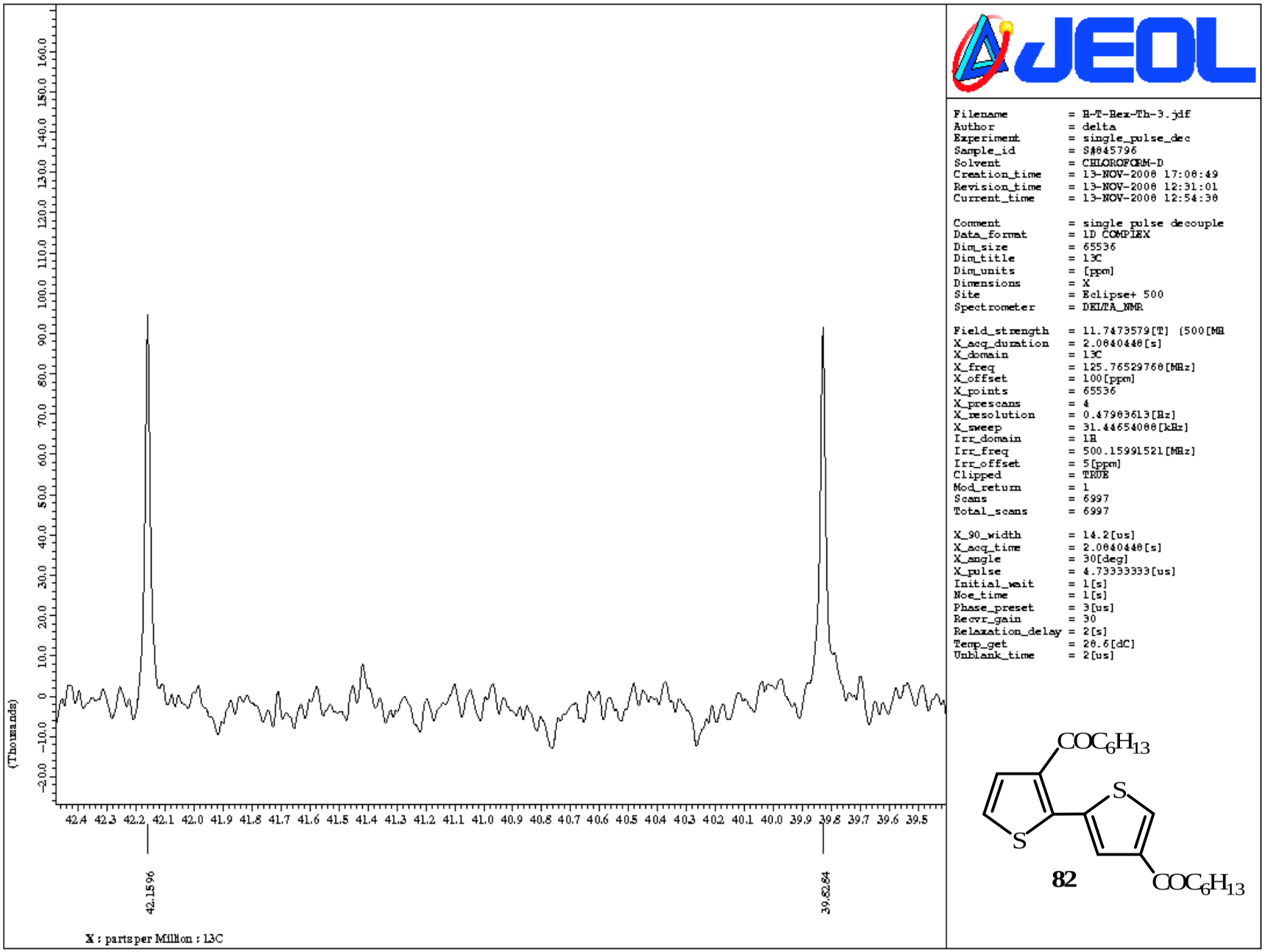

```
Filename          = H-T-Hex-Th-3.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#045796
Solvent           = CHLOROFORM-D
Creation_time     = 13-NOV-2008 17:08:49
Revision_time     = 13-NOV-2008 12:31:01
Current_time      = 13-NOV-2008 12:43:07

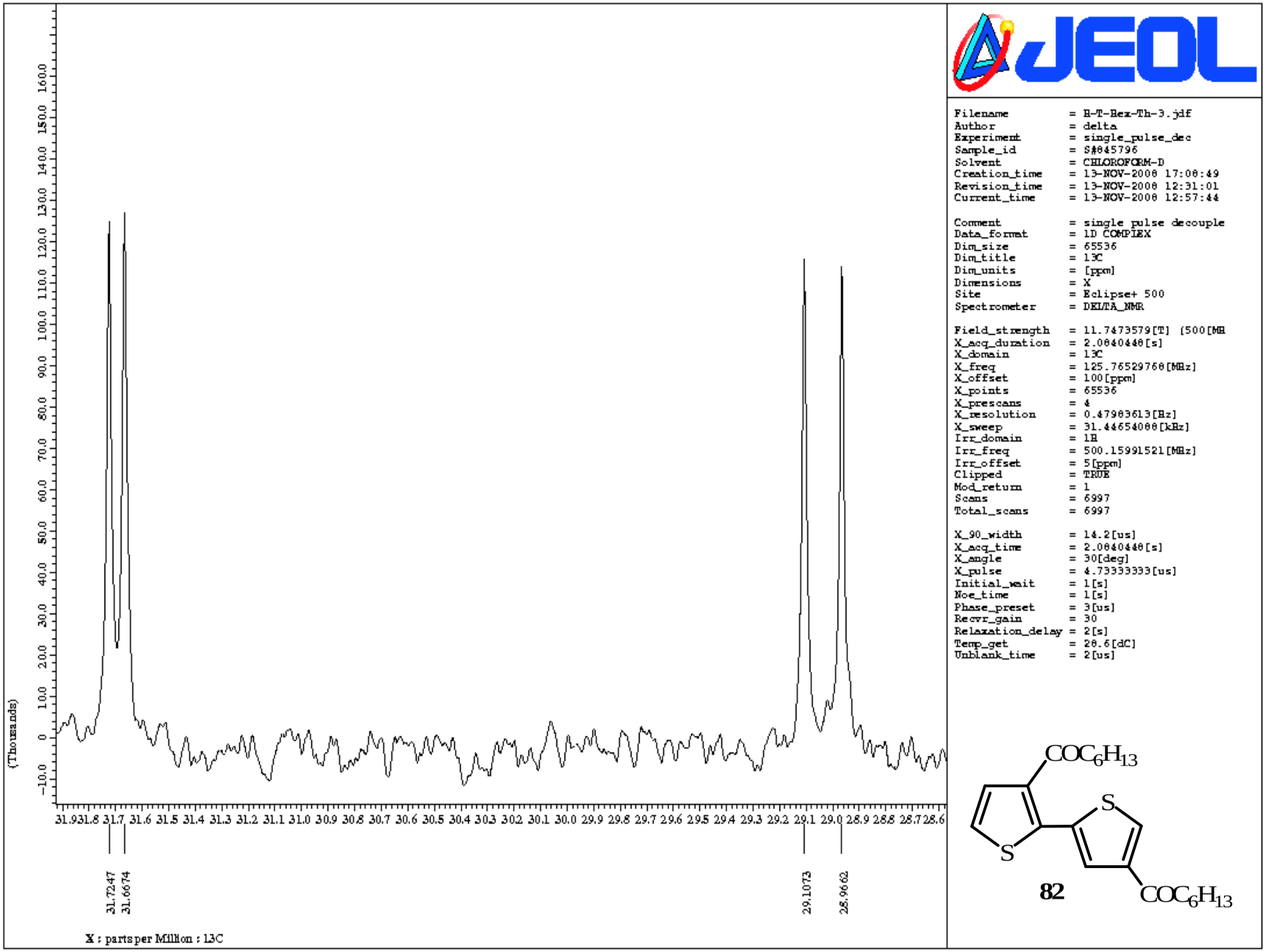
Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 65536
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 2.0840448[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 65536
X_prescans        = 4
X_resolution      = 0.47983613[Hz]
X_sweep           = 31.44654088[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5[ppm]
Clipped           = TRUE
Mod_return        = 1
Scans             = 6997
Total_scans       = 6997

X_90_width        = 14.2[us]
X_acq_time        = 2.0840448[s]
X_angle           = 30[deg]
X_pulse           = 4.73333333[us]
Initial_wait      = 1[s]
Noe_time          = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 30
Relaxation_delay  = 2[s]
Temp_get          = 28.6[dC]
Unblank_time      = 2[us]
```


82


(Thousands)
42.1596
39.8284
X : parts per Million : 13C
Filename = H-T-Hex-Th-3.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = S#045796
Solvent = CHLOROFORM-D
Creation_time = 13-NOV-2008 17:08:49
Revision_time = 13-NOV-2008 12:31:01
Current_time = 13-NOV-2008 12:54:38
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 65536
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.0840448[s]
X_domain = 13C
X_freq = 125.76529760[MHz]
X_offset = 100[ppm]
X_points = 65536
X_prescans = 4
X_resolution = 0.47983613[Hz]
X_sweep = 31.44654088[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5[ppm]
Clipped = TRUE
Mod_return = 1
Scans = 6997
Total_scans = 6997
X_90_width = 14.2[us]
X_acq_time = 2.0840448[s]
X_angle = 30[deg]
X_pulse = 4.73333333[us]
Initial_wait = 1[s]
Noe_time = 1[s]
Phase_preset = 3[us]
Recvr_gain = 30
Relaxation_delay = 2[s]
Temp_get = 20.6[dC]
Unblank_time = 2[us]
COC6H13
S
S
COC6H13
82



JEOL

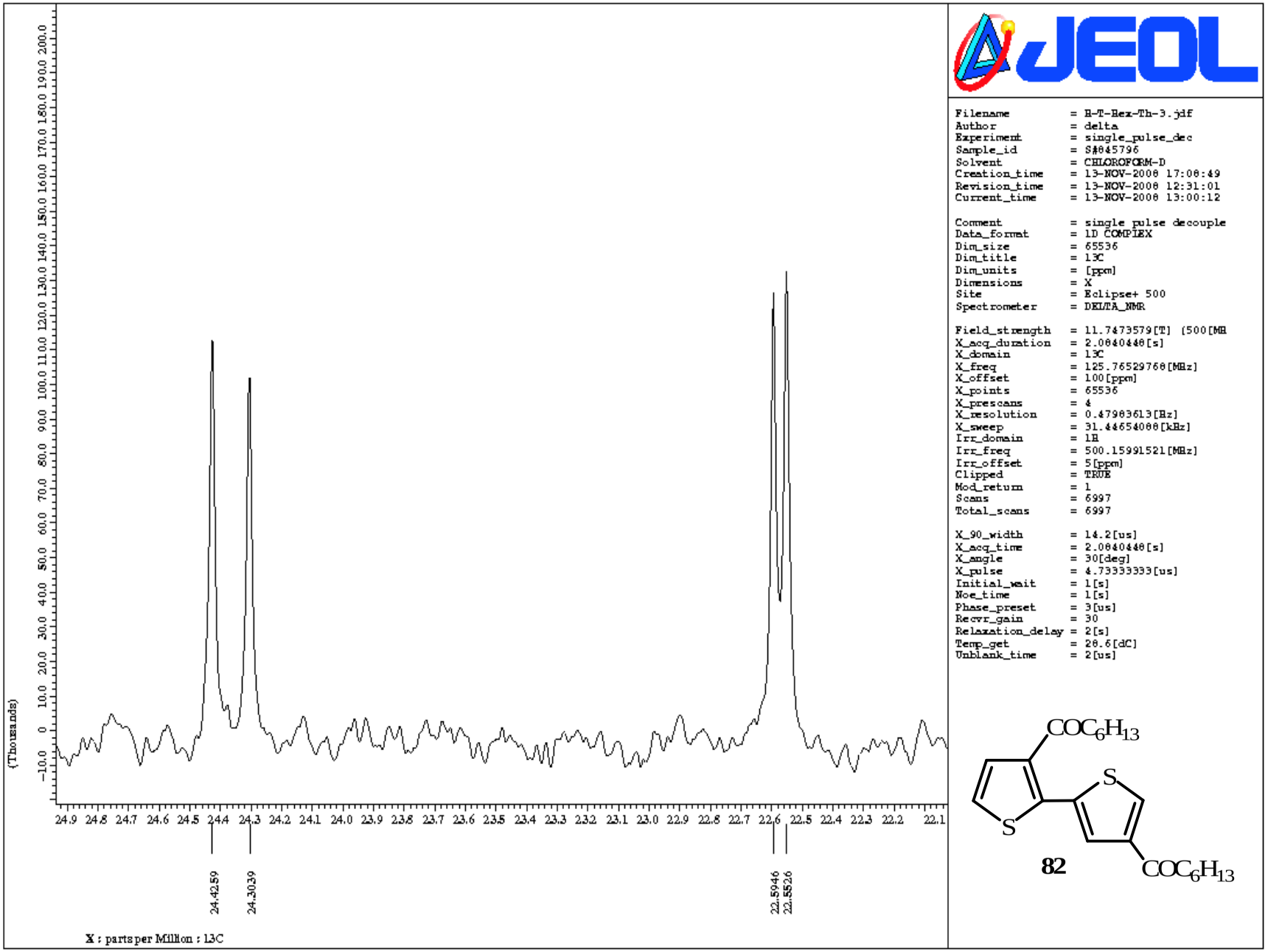
```
Filename          = H-T-Hex-Th-3.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#845796
Solvent           = CHLOROFORM-D
Creation_time     = 13-NOV-2008 17:08:49
Revision_time     = 13-NOV-2008 12:31:01
Current_time      = 13-NOV-2008 12:57:44

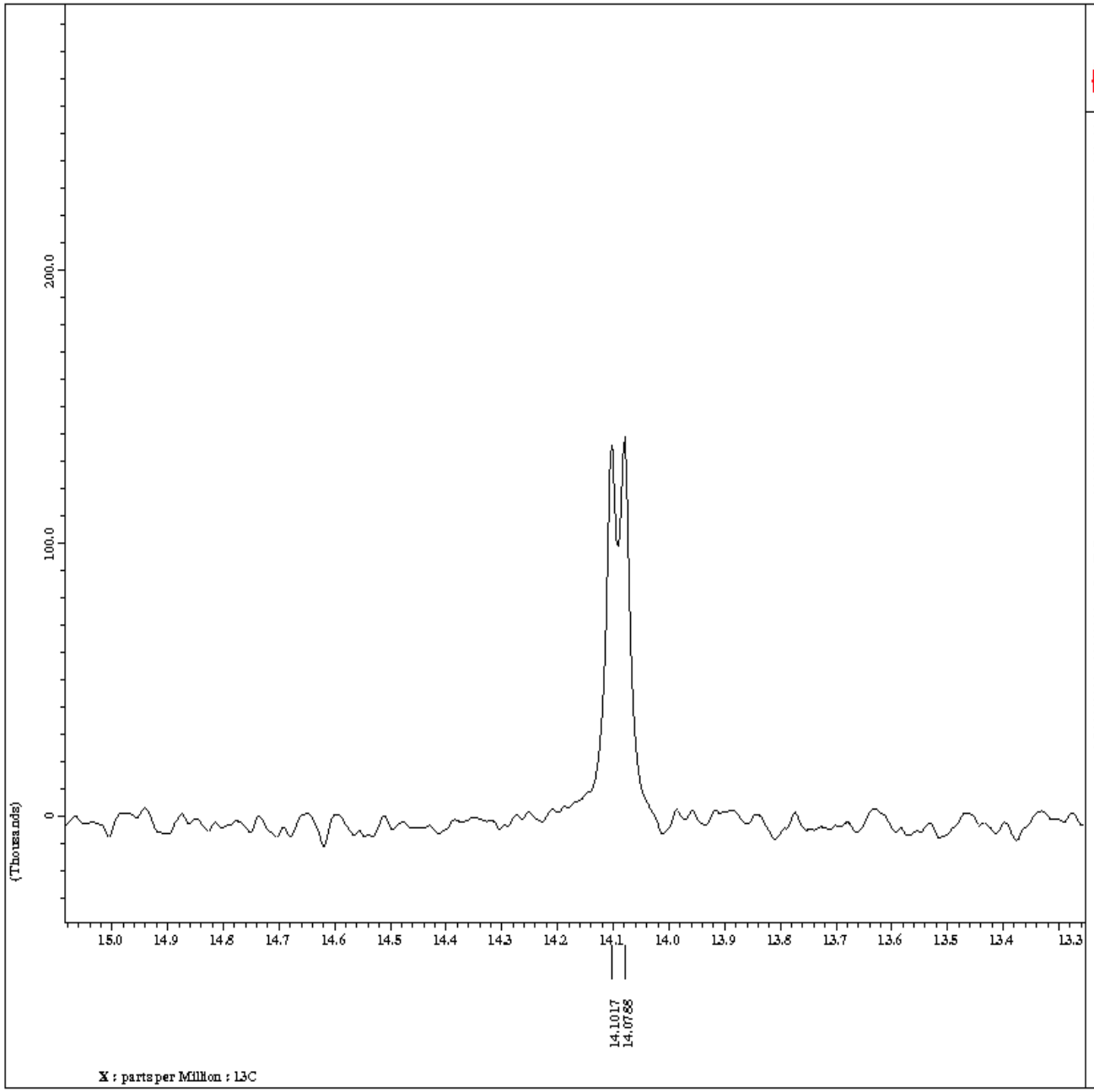
Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 65536
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 2.0840448[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 65536
X_prescans        = 4
X_resolution      = 0.47983613[Hz]
X_sweep           = 31.44654088[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5[ppm]
Clipped           = TRUE
Mod_return        = 1
Scans             = 6997
Total_scans       = 6997

X_90_width        = 14.2[us]
X_acq_time        = 2.0840448[s]
X_angle           = 30[deg]
X_pulse           = 4.73333333[us]
Initial_wait      = 1[s]
Noe_time          = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 30
Relaxation_delay  = 2[s]
Temp_get          = 28.6[dC]
Unblank_time      = 2[us]
```


82


(Thousands)
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
24.9 24.8 24.7 24.6 24.5 24.4 24.3 24.2 24.1 24.0 23.9 23.8 23.7 23.6 23.5 23.4 23.3 23.2 23.1 23.0 22.9 22.8 22.7 22.6 22.5 22.4 22.3 22.2 22.1
24.4259
24.3039
22.5946
22.5526
X : parts per Million : 13C
Filename = H-T-Hex-Th-3.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = S#045796
Solvent = CHLOROFORM-D
Creation_time = 13-NOV-2008 17:08:49
Revision_time = 13-NOV-2008 12:31:01
Current_time = 13-NOV-2008 13:00:12
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 65536
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.0840448[s]
X_domain = 13C
X_freq = 125.76529768[MHz]
X_offset = 100[ppm]
X_points = 65536
X_prescans = 4
X_resolution = 0.47983613[Hz]
X_sweep = 31.44654088[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5[ppm]
Clipped = TRUE
Mod_return = 1
Scans = 6997
Total_scans = 6997
X_90_width = 14.2[us]
X_acq_time = 2.0840448[s]
X_angle = 30[deg]
X_pulse = 4.73333333[us]
Initial_wait = 1[s]
Noe_time = 1[s]
Phase_preset = 3[us]
Recvr_gain = 30
Relaxation_delay = 2[s]
Temp_get = 28.6[dC]
Unblank_time = 2[us]
COC6H13
S
S
COC6H13
82



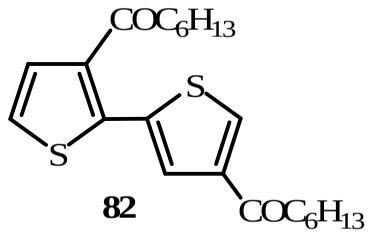
JEOL

```
Filename          = H-T-Hex-Th-3.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#0&5796
Solvent           = CHLOROFORM-D
Creation_time     = 13-NOV-2008 17:08:49
Revision_time     = 13-NOV-2008 12:31:01
Current_time      = 13-NOV-2008 13:00:57

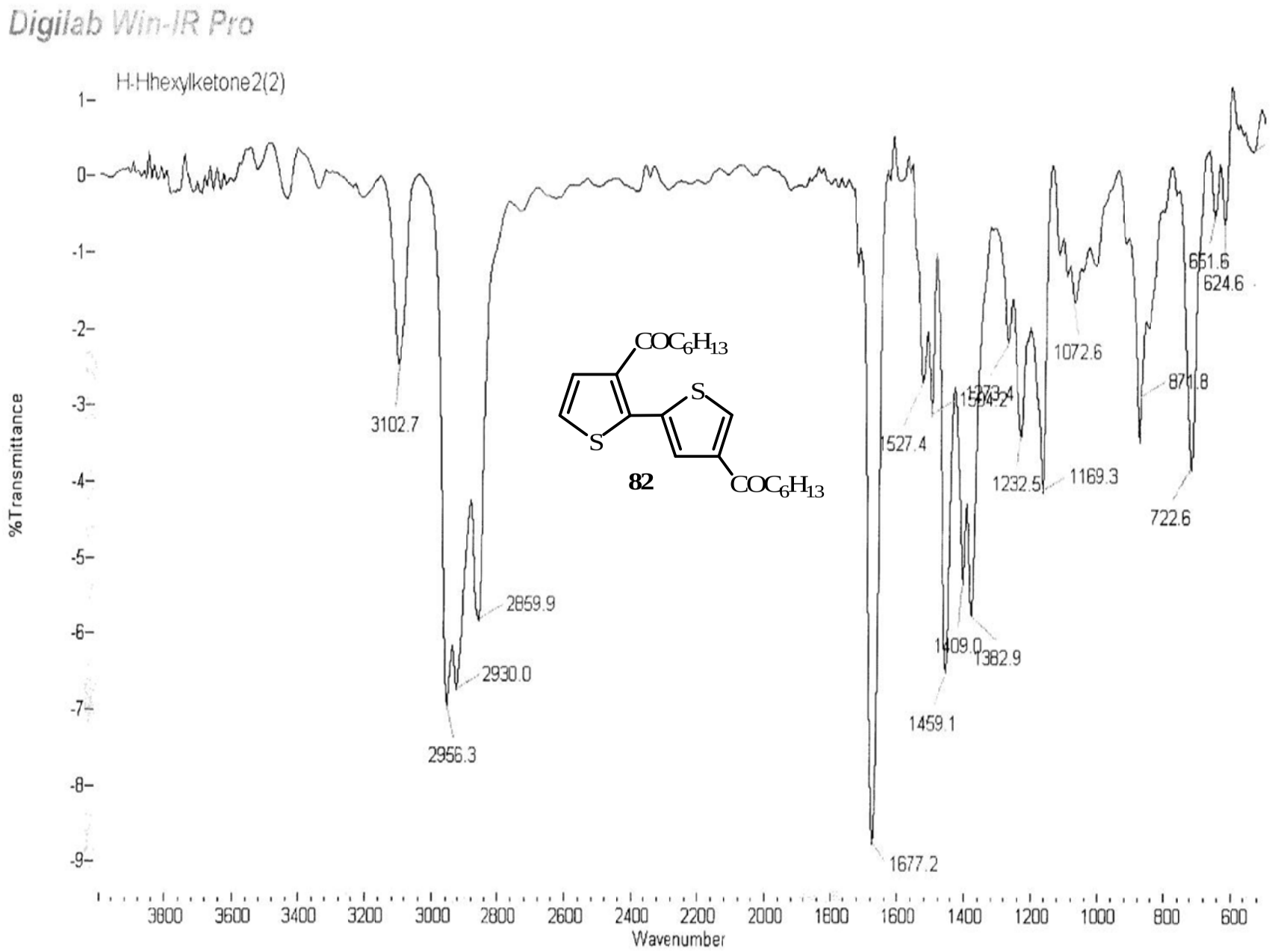
Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 65536
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 2.0840448[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 65536
X_prescans        = 4
X_resolution      = 0.47983613[Hz]
X_sweep           = 31.44654088[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5[ppm]
Clipped           = TRUE
Mod_return        = 1
Scans             = 6997
Total_scans       = 6997

X_90_width        = 14.2[us]
X_acq_time        = 2.0840448[s]
X_angle           = 30[deg]
X_pulse           = 4.73333333[us]
Initial_wait      = 1[s]
Noe_time          = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 30
Relaxation_delay  = 2[s]
Temp_get          = 28.6[dC]
Unblank_time      = 2[us]
```

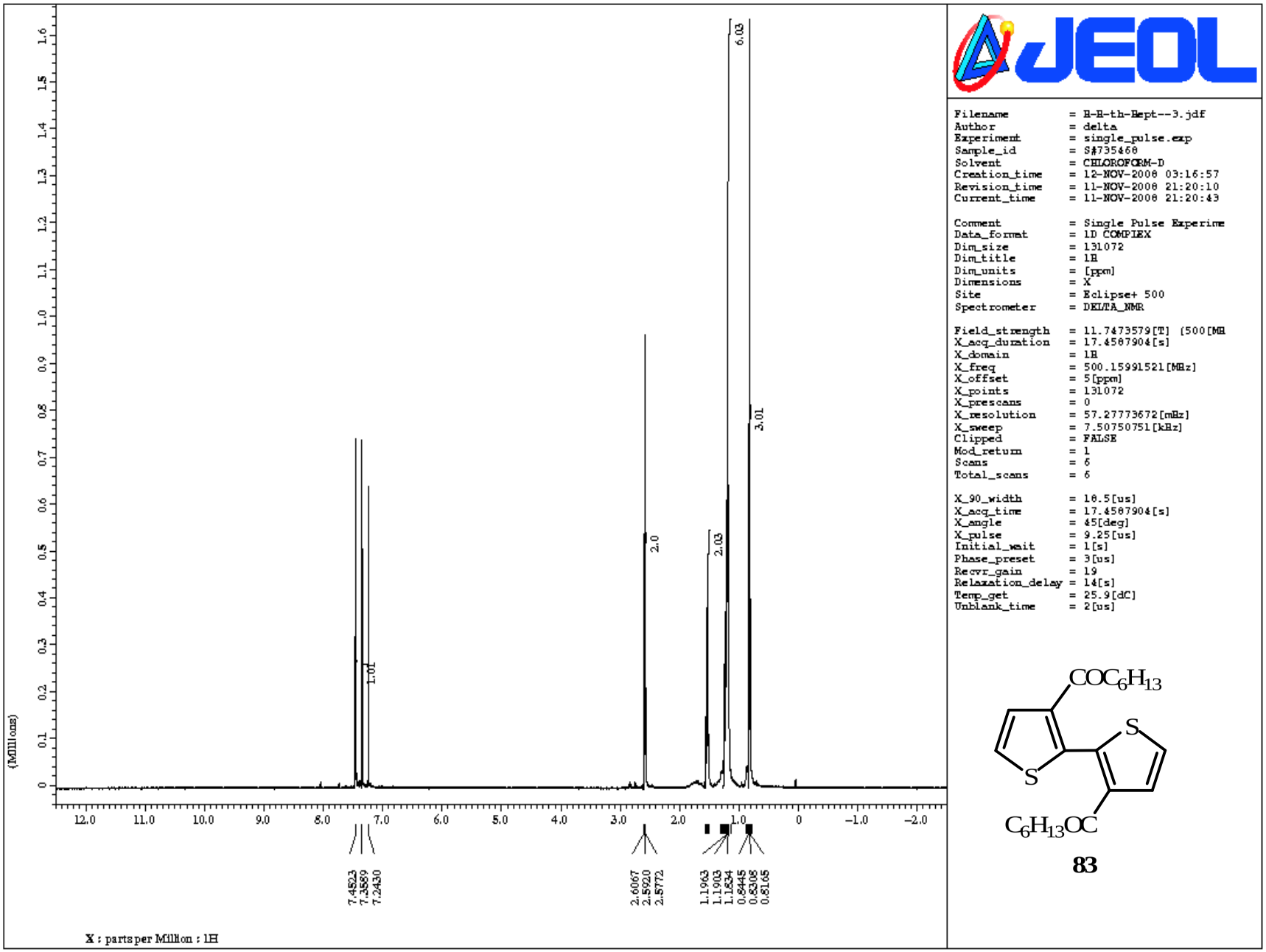


82


Digilab Win-IR Pro
H-Hhexylketone2(2)
%Transmittance
Wavenumber
3102.7
2956.3
2930.0
2859.9
1677.2
1527.4
1459.1
1409.0
1382.9
1273.4
1232.5
1169.3
1072.6
722.6
651.6
624.6
82

APPENDIX 9

^{1}H, ^{13}C NMR and IR spectra of 3,3'-diyl)diheptanoyl -2,2'-bithiophene (**83**)



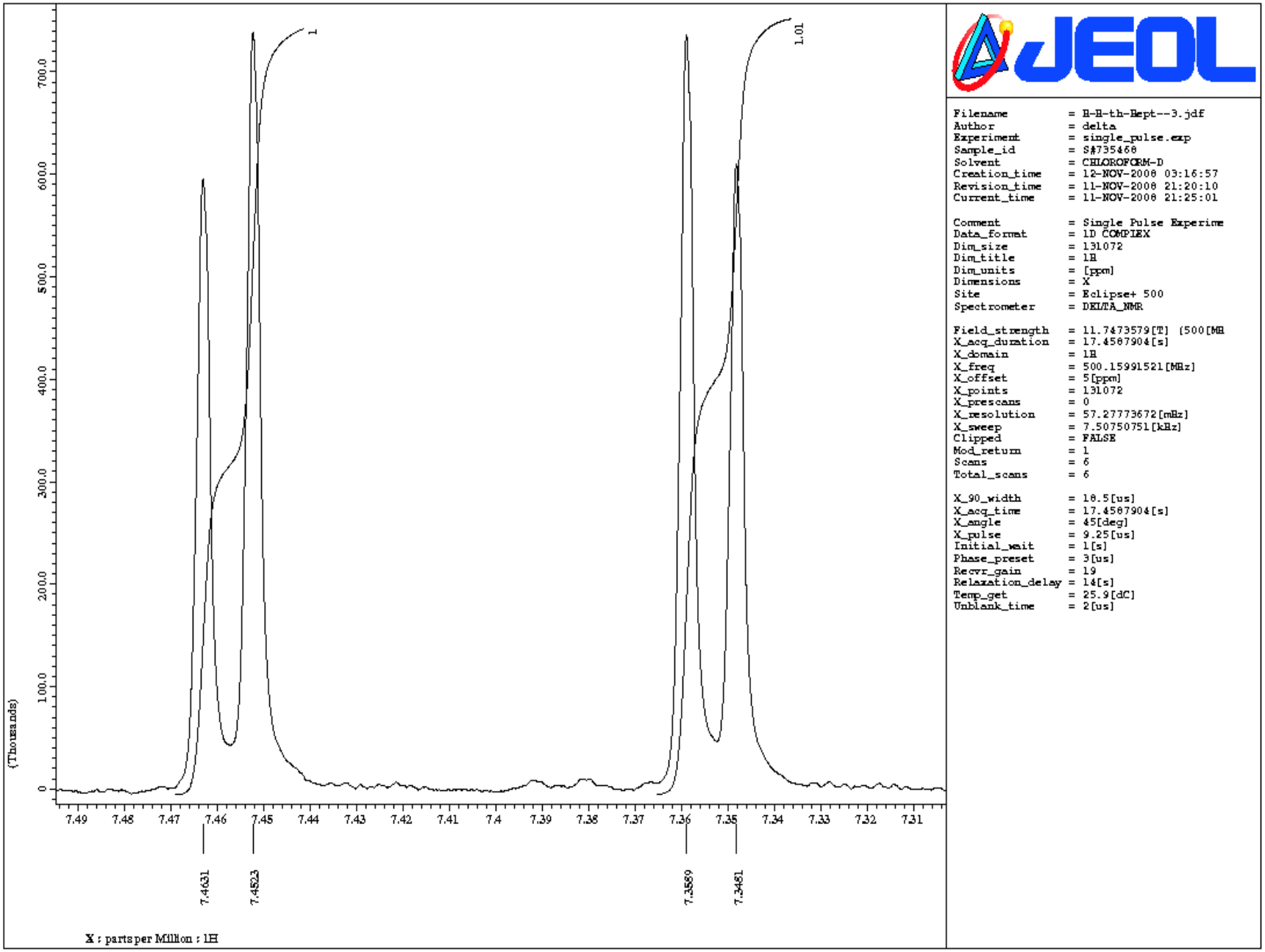
Filename = H-H-th-Hept--3.jdf
Author = delta
Experiment = single_pulse.exp
Sample_id = S#735468
Solvent = CHLOROFORM-D
Creation_time = 12-NOV-2008 03:16:57
Revision_time = 11-NOV-2008 21:20:10
Current_time = 11-NOV-2008 21:20:43

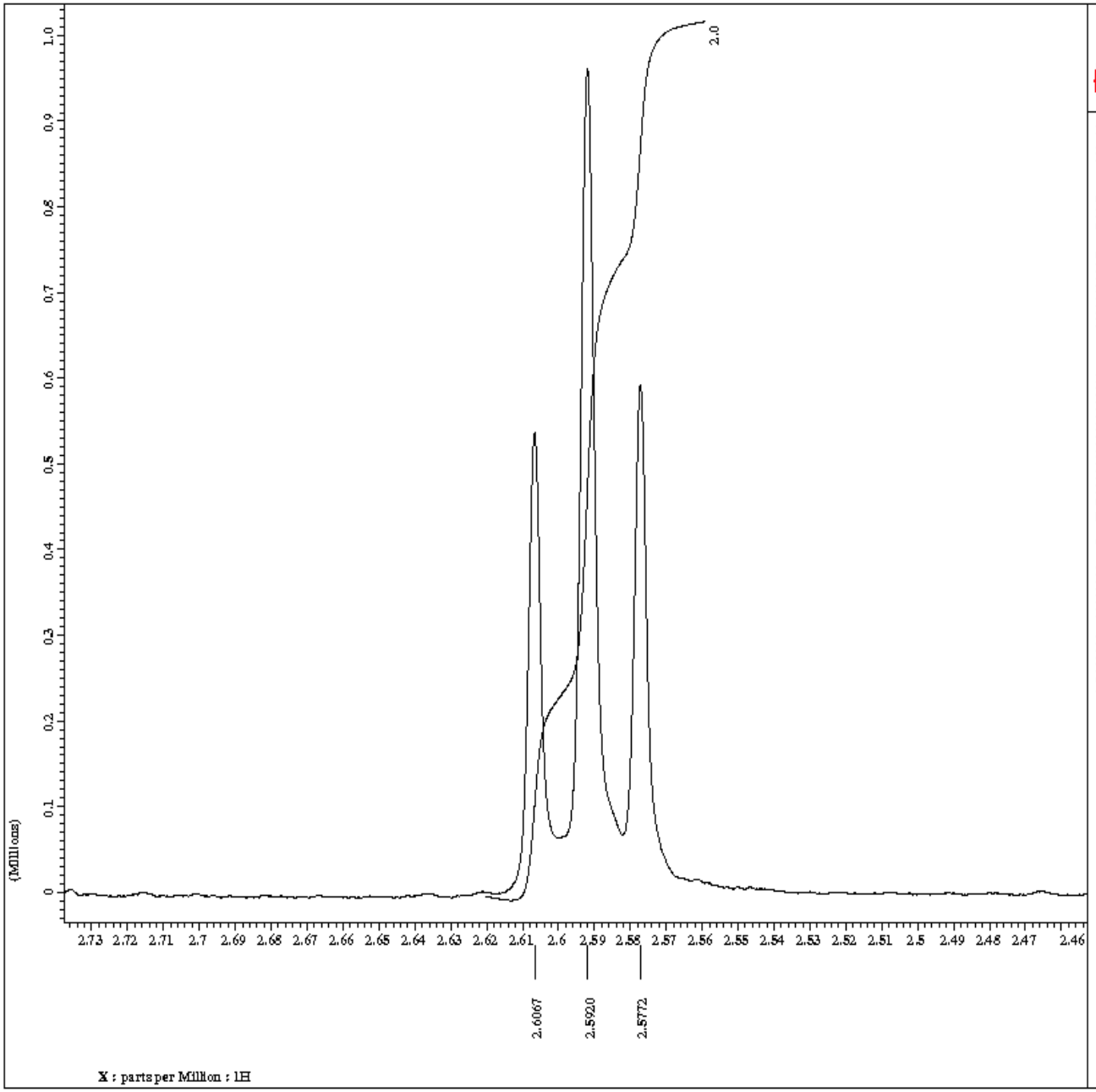
Comment = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 131072
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR

Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 17.4587904[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 131072
X_prescans = 0
X_resolution = 57.27773672[mHz]
X_sweep = 7.50750751[kHz]
Clipped = FALSE
Mod_return = 1
Scans = 6
Total_scans = 6

X_90_width = 18.5[us]
X_acq_time = 17.4587904[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 19
Relaxation_delay = 14[s]
Temp_get = 25.9[dC]
Unblank_time = 2[us]

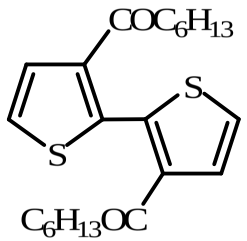
83


1
1.01
700.0
600.0
500.0
400.0
300.0
200.0
100.0
0
(Thousands)
7.49
7.48
7.47
7.46
7.45
7.44
7.43
7.42
7.41
7.4
7.39
7.38
7.37
7.36
7.35
7.34
7.33
7.32
7.31
7.4631
7.4523
7.3589
7.3481
X : parts per Million : 1H
JEOL
Filename = H-H-th-Hept--3.jdf
Author = delta
Experiment = single_pulse.exp
Sample_id = S#735&60
Solvent = CHLOROFORM-D
Creation_time = 12-NOV-2008 03:16:57
Revision_time = 11-NOV-2008 21:20:10
Current_time = 11-NOV-2008 21:25:01
Comment = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 131072
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 17.4567904[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 131072
X_prescans = 0
X_resolution = 57.27773672[mHz]
X_sweep = 7.50750751[kHz]
Clipped = FALSE
Mod_return = 1
Scans = 6
Total_scans = 6
X_90_width = 18.5[us]
X_acq_time = 17.4567904[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 19
Relaxation_delay = 14[s]
Temp_get = 25.9[dC]
Unblank_time = 2[us]

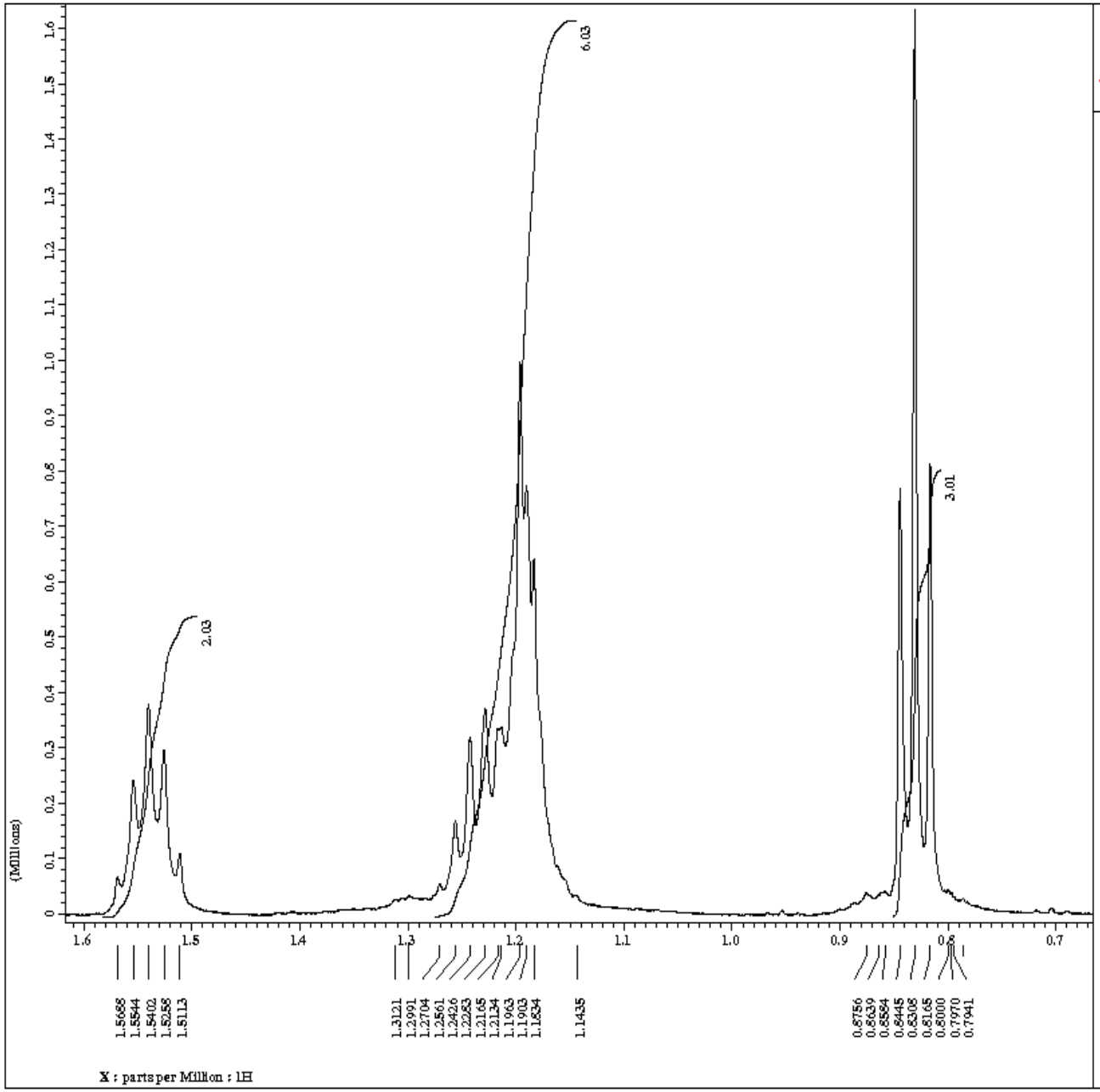


JEOL

Filename	= R-R-th-Hept--3.jdf
Author	= delta
Experiment	= single_pulse.exp
Sample_id	= S#735468
Solvent	= CHLOROFORM-D
Creation_time	= 12-NOV-2008 03:16:57
Revision_time	= 11-NOV-2008 21:20:10
Current_time	= 11-NOV-2008 21:29:05
Comment	= Single Pulse Experime
Data_format	= 1D COMPLEX
Dim_size	= 131072
Dim_title	= 1H
Dim_units	= [ppm]
Dimensions	= X
Site	= Eclipse+ 500
Spectrometer	= DELTA_NMR
Field_strength	= 11.7473579[T] (500[MH
X_acq_duration	= 17.4587904[s]
X_domain	= 1H
X_freq	= 500.15991521[MHz]
X_offset	= 5[ppm]
X_points	= 131072
X_prescans	= 0
X_resolution	= 57.27773672[mHz]
X_sweep	= 7.50750751[kHz]
Clipped	= FALSE
Mod_return	= 1
Scans	= 6
Total_scans	= 6
X_90_width	= 10.5[us]
X_acq_time	= 17.4587904[s]
X_angle	= 45[deg]
X_pulse	= 9.25[us]
Initial_wait	= 1[s]
Phase_preset	= 3[us]
Recvr_gain	= 19
Relaxation_delay	= 14[s]
Temp_get	= 25.9[dC]
Unblank_time	= 2[us]



83



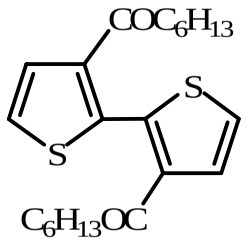
JEOL

```
Filename          = H-H-th-Hept--3.jdf
Author            = delta
Experiment        = single_pulse.exp
Sample_id         = S#735&60
Solvent           = CHLOROFORM-D
Creation_time     = 12-NOV-2008 03:16:57
Revision_time     = 11-NOV-2008 21:20:10
Current_time      = 11-NOV-2008 21:32:19

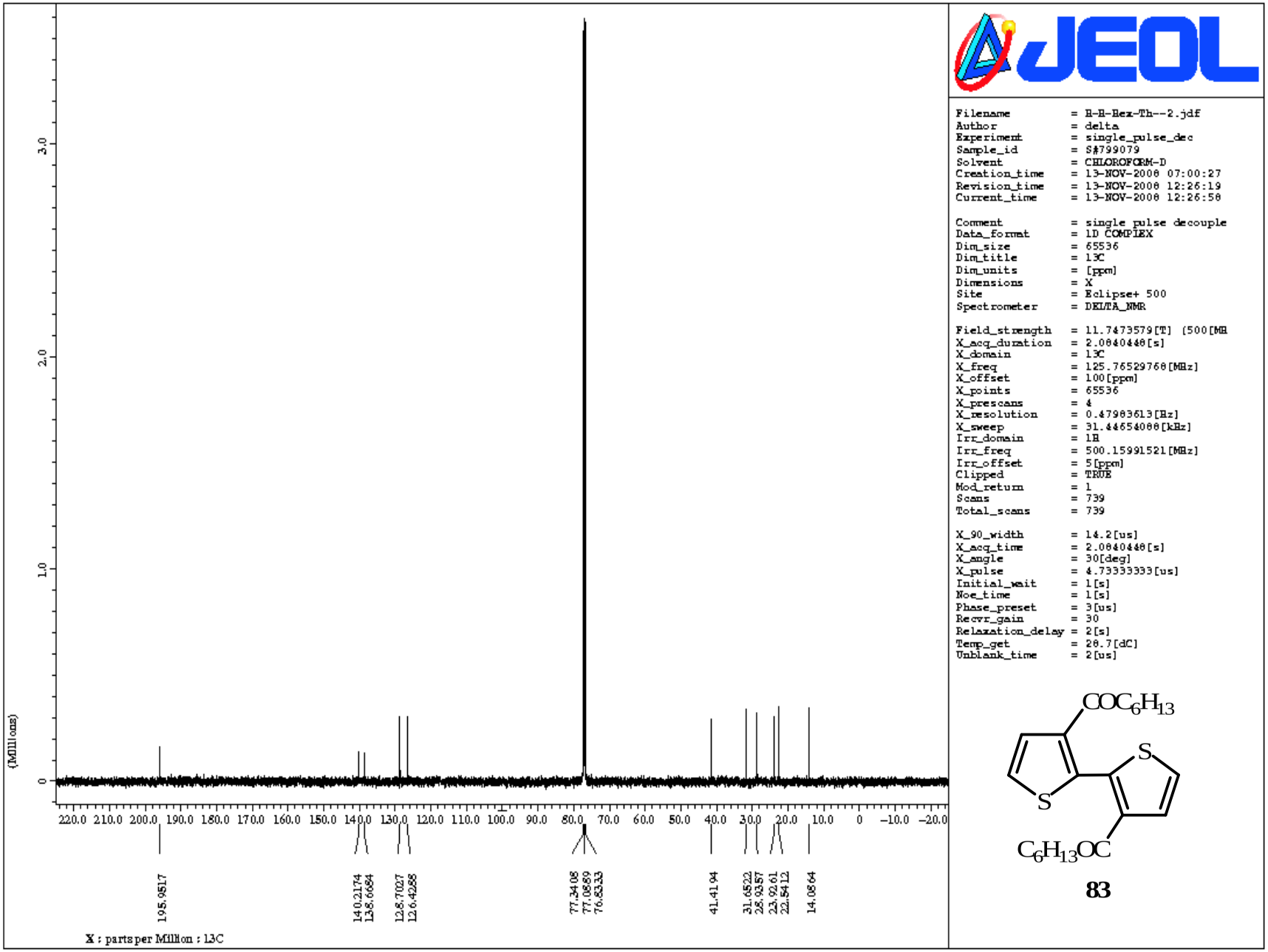
Comment           = Single Pulse Experime
Data_format       = 1D COMPLEX
Dim_size          = 131072
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

Field_strength    = 11.7473579[T]  (500[MH
X_acq_duration    = 17.4587904[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 5[ppm]
X_points          = 131072
X_prescans        = 0
X_resolution      = 57.27773672[mHz]
X_sweep           = 7.50750751[kHz]
Clipped           = FALSE
Mod_return        = 1
Scans             = 6
Total_scans       = 6

X_90_width        = 10.5[us]
X_acq_time        = 17.4587904[s]
X_angle           = 45[deg]
X_pulse           = 9.25[us]
Initial_wait      = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 19
Relaxation_delay  = 14[s]
Temp_get          = 25.9[dC]
Unblank_time      = 2[us]
```



83



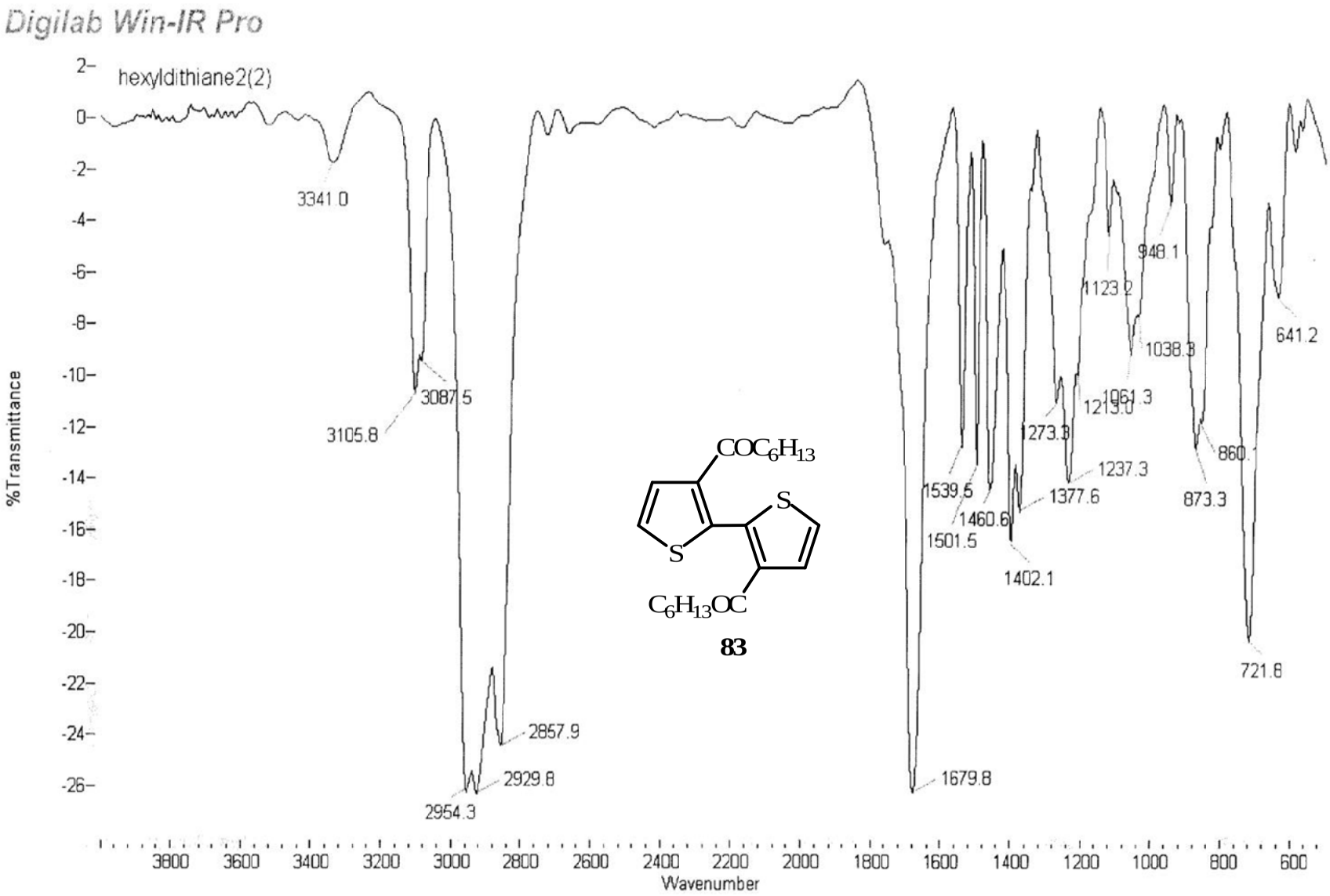
Filename = H-H-Hex-Th--2.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = S#799079
Solvent = CHLOROFORM-D
Creation_time = 13-NOV-2008 07:00:27
Revision_time = 13-NOV-2008 12:26:19
Current_time = 13-NOV-2008 12:26:58

Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 65536
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR

Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.0840448[s]
X_domain = 13C
X_freq = 125.76529768[MHz]
X_offset = 100[ppm]
X_points = 65536
X_prescans = 4
X_resolution = 0.47983613[Hz]
X_sweep = 31.44654088[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5[ppm]
Clipped = TRUE
Mod_return = 1
Scans = 739
Total_scans = 739

X_90_width = 14.2[us]
X_acq_time = 2.0840448[s]
X_angle = 30[deg]
X_pulse = 4.73333333[us]
Initial_wait = 1[s]
Noe_time = 1[s]
Phase_preset = 3[us]
Recvr_gain = 30
Relaxation_delay = 2[s]
Temp_get = 28.7[dC]
Unblank_time = 2[us]

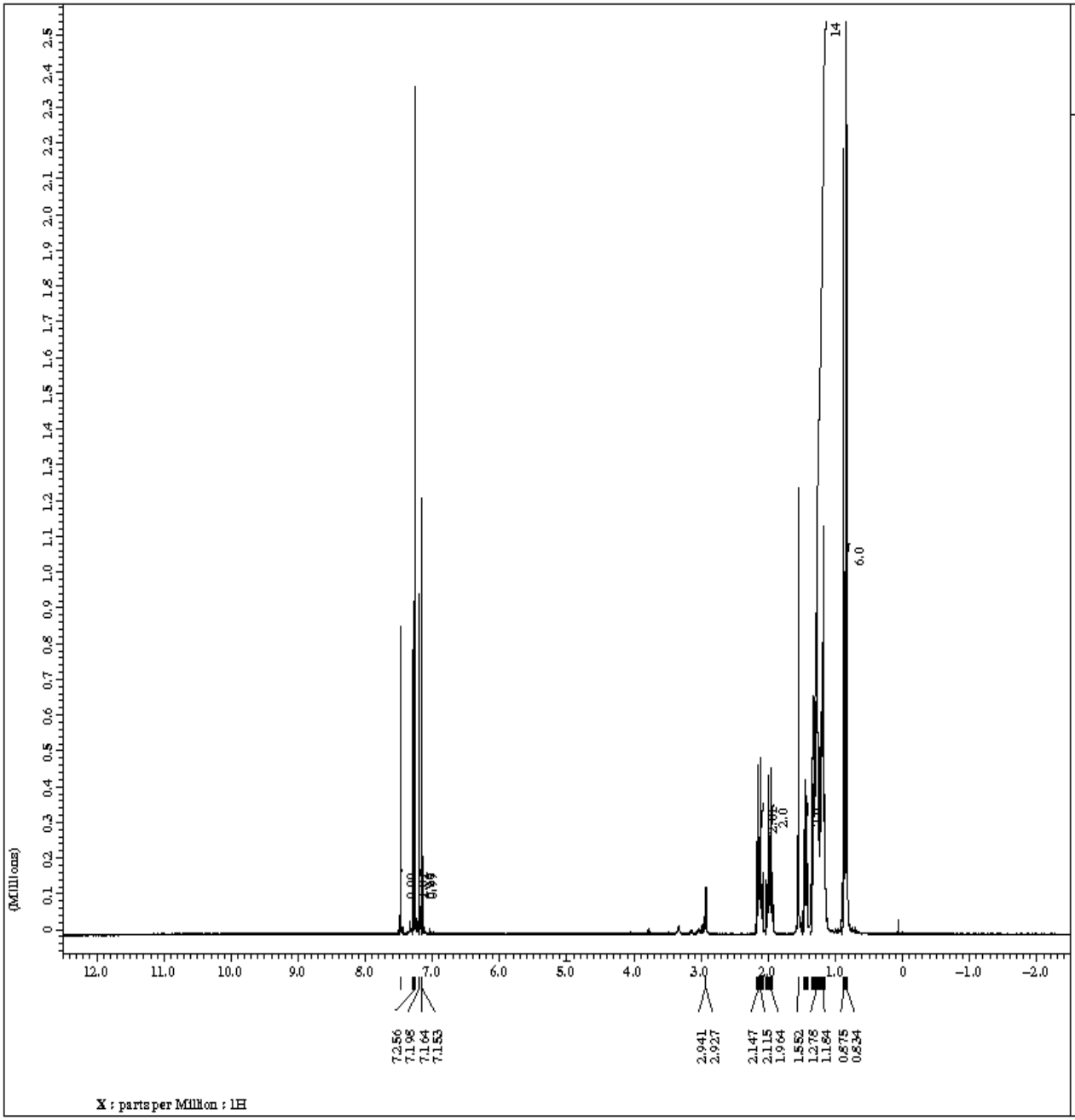
83

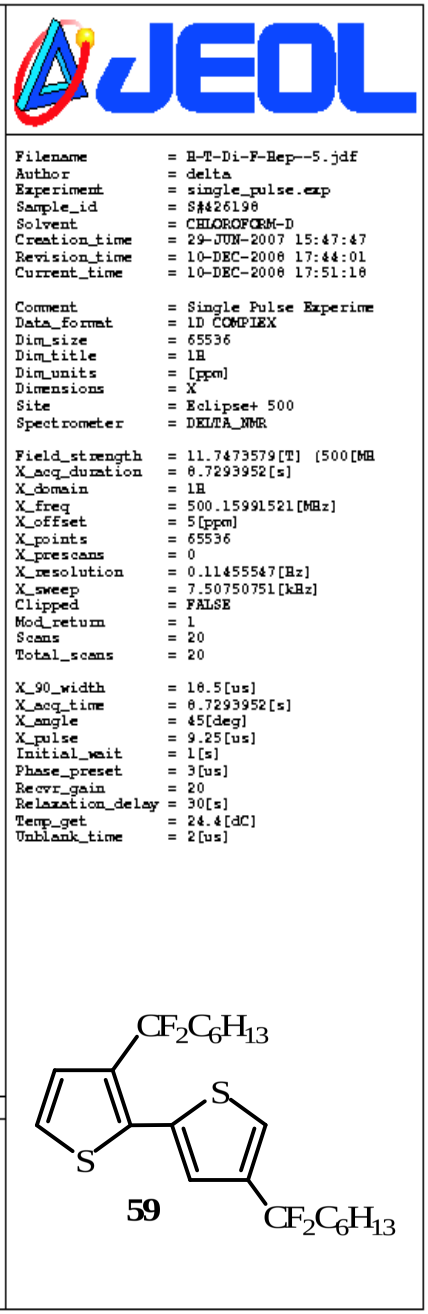

Digilab Win-IR Pro
hexyldithiane2(2)
%Transmittance
Wavenumber
3341.0
3105.8
3087.5
2954.3
2929.8
2857.9
1679.8
1539.5
1501.5
1460.6
1402.1
1377.6
1273.3
1237.3
1213.0
1123.2
1061.3
1038.3
948.1
873.3
860.1
721.8
641.2
COC_6H_{13}
$C_6H_{13}OC$
S
S

83

APPENDIX 10

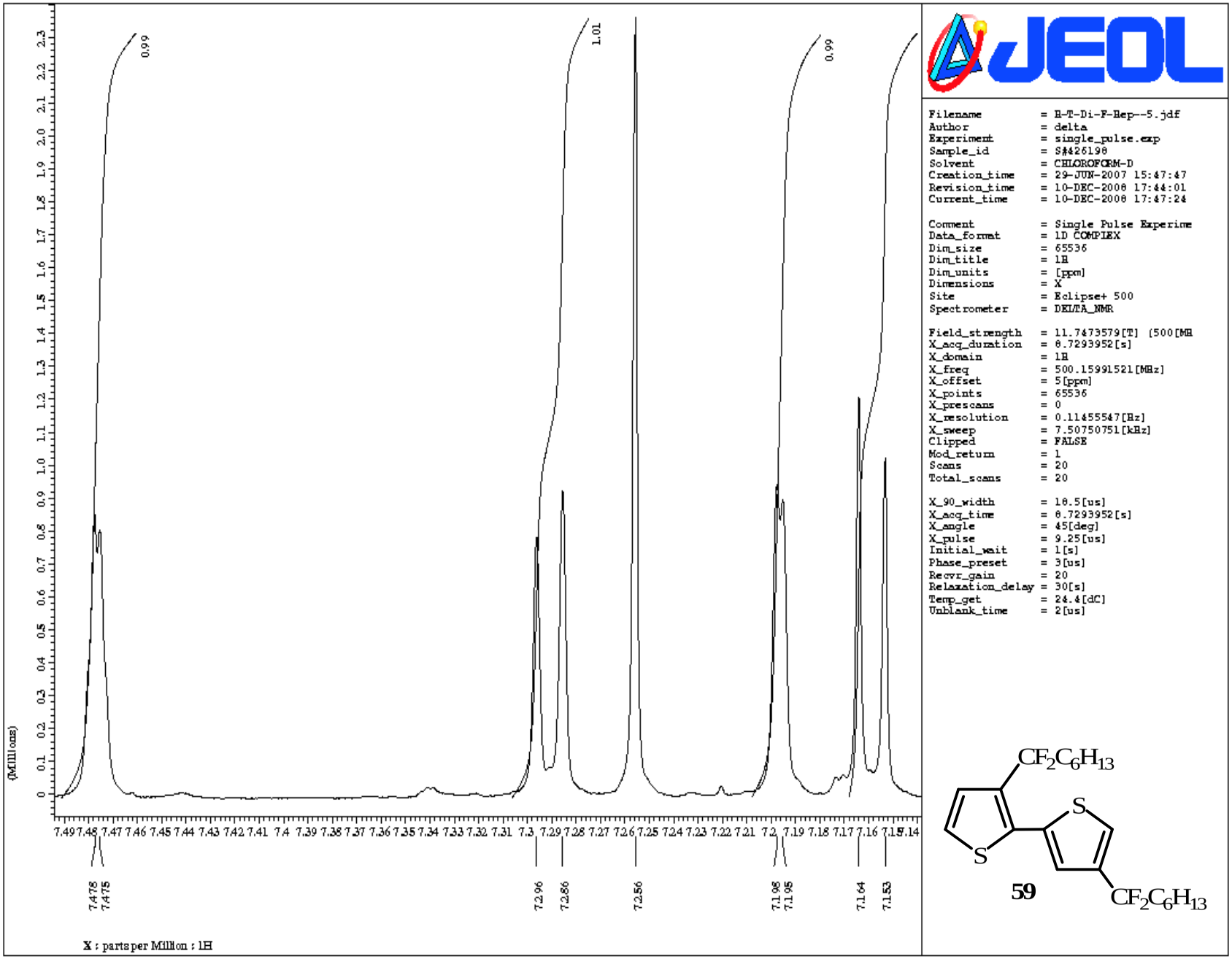
^{1}H, ^{13}C, ^{19}F NMR and IR spectra of 3,4'-bis(1,1-difluoroheptyl)-2,2'-bithiophene (**59**)

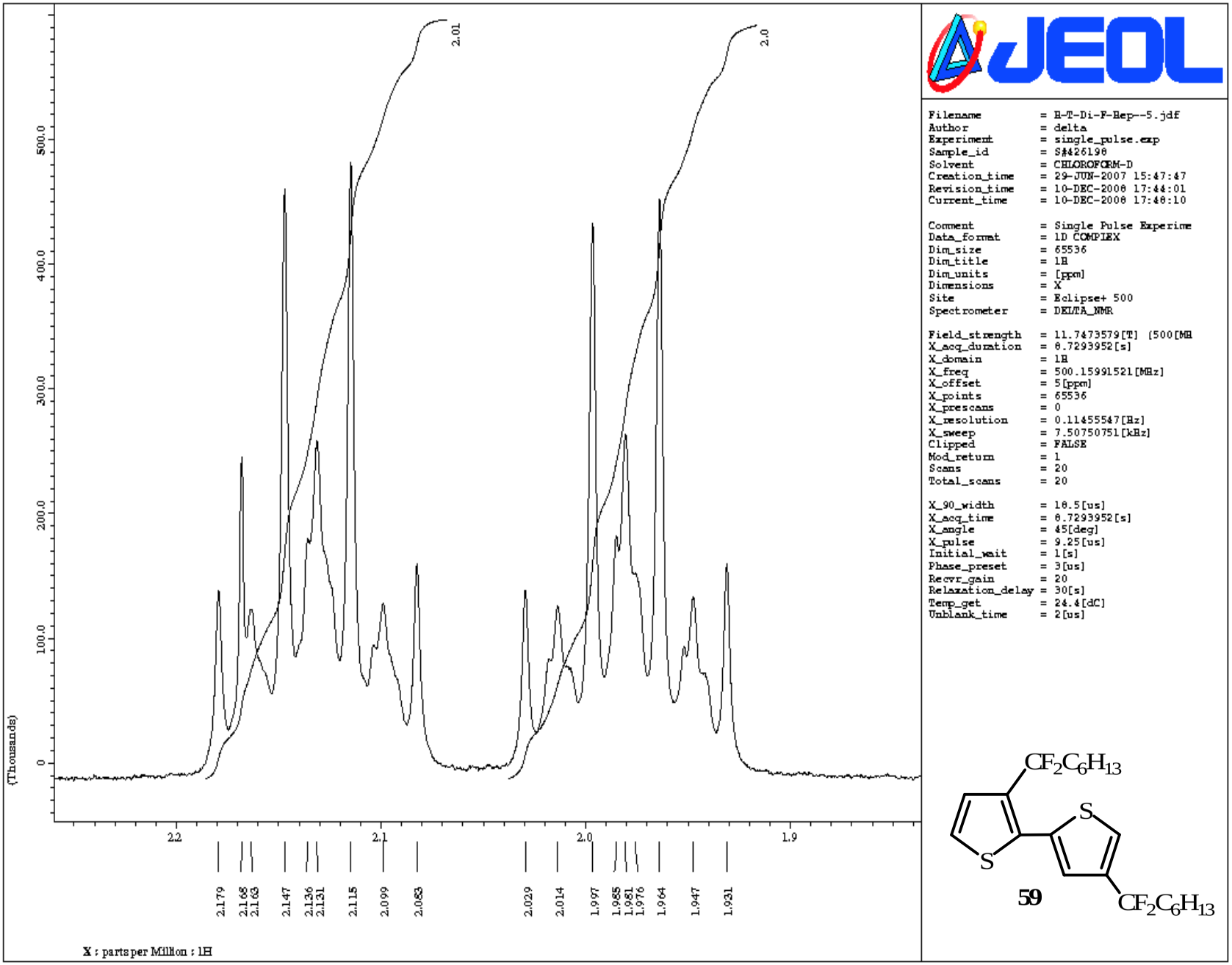

(Millions)
14
6.0
2.0
7.256
7.198
7.164
7.153
2.941
2.927
2.147
2.115
1.964
1.552
1.278
1.184
0.875
0.834
X : parts per Million : 1H


Filename = H-T-Di-F-Hep--5.jdf
Author = delta
Experiment = single_pulse.exp
Sample_id = S#426198
Solvent = CHLOROFORM-D
Creation_time = 29-JUN-2007 15:47:47
Revision_time = 10-DEC-2008 17:44:01
Current_time = 10-DEC-2008 17:51:18
Comment = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 65536
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 0.7293952[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 65536
X_prescans = 0
X_resolution = 0.11455547[Hz]
X_sweep = 7.50750751[kHz]
Clipped = FALSE
Mod_return = 1
Scans = 20
Total_scans = 20
X_90_width = 10.5[us]
X_acq_time = 0.7293952[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 20
Relaxation_delay = 30[s]
Temp_get = 24.4[dC]
Unblank_time = 2[us]

CF2C6H13
S
S
CF2C6H13

59


0.99
1.01
0.99
(Millions)
7.49 7.48 7.47 7.46 7.45 7.44 7.43 7.42 7.41 7.4 7.39 7.38 7.37 7.36 7.35 7.34 7.33 7.32 7.31 7.3 7.29 7.28 7.27 7.26 7.25 7.24 7.23 7.22 7.21 7.2 7.19 7.18 7.17 7.16 7.15 7.14
7.478
7.475
7.296
7.286
7.256
7.198
7.195
7.164
7.153
X : parts per Million : 1H
JEOL
Filename = B-T-Di-F-Hep--5.jdf
Author = delta
Experiment = single_pulse.exp
Sample_id = S#426198
Solvent = CHLOROFORM-D
Creation_time = 29-JUN-2007 15:47:47
Revision_time = 10-DEC-2008 17:44:01
Current_time = 10-DEC-2008 17:47:24
Comment = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 65536
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 0.7293952[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 65536
X_prescans = 0
X_resolution = 0.11455547[Hz]
X_sweep = 7.50750751[kHz]
Clipped = FALSE
Mod_return = 1
Scans = 20
Total_scans = 20
X_90_width = 10.5[us]
X_acq_time = 0.7293952[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 20
Relaxation_delay = 30[s]
Temp_get = 24.4[dC]
Unblank_time = 2[us]
CF2C6H13
S
S
CF2C6H13
59



JEOL

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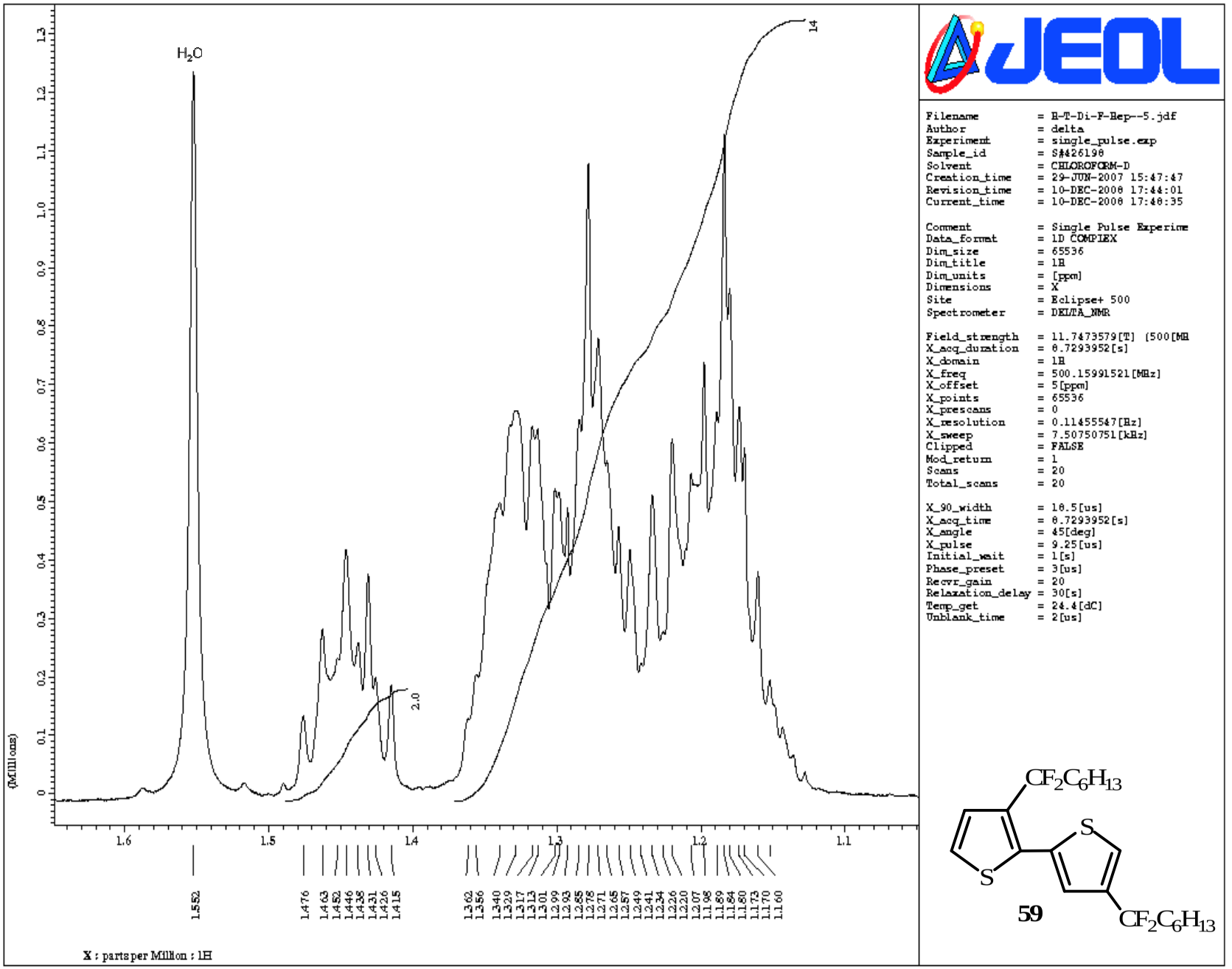
Filename          = H-T-Di-F-Hep--5.jdf
Author            = delta
Experiment        = single_pulse.exp
Sample_id         = S#426190
Solvent           = CHLOROFORM-D
Creation_time     = 29-JUN-2007 15:47:47
Revision_time     = 10-DEC-2008 17:44:01
Current_time      = 10-DEC-2008 17:48:10

Comment           = Single Pulse Experime
Data_format       = 1D COMPLEX
Dim_size          = 65536
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 0.7293952[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 5[ppm]
X_points          = 65536
X_prescans        = 0
X_resolution      = 0.11455547[Hz]
X_sweep           = 7.50750751[kHz]
Clipped           = FALSE
Mod_return        = 1
Scans             = 20
Total_scans       = 20

X_90_width        = 10.5[us]
X_acq_time        = 0.7293952[s]
X_angle           = 45[deg]
X_pulse           = 9.25[us]
Initial_wait      = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 20
Relaxation_delay  = 30[s]
Temp_get          = 24.4[dC]
Unblank_time      = 2[us]
```

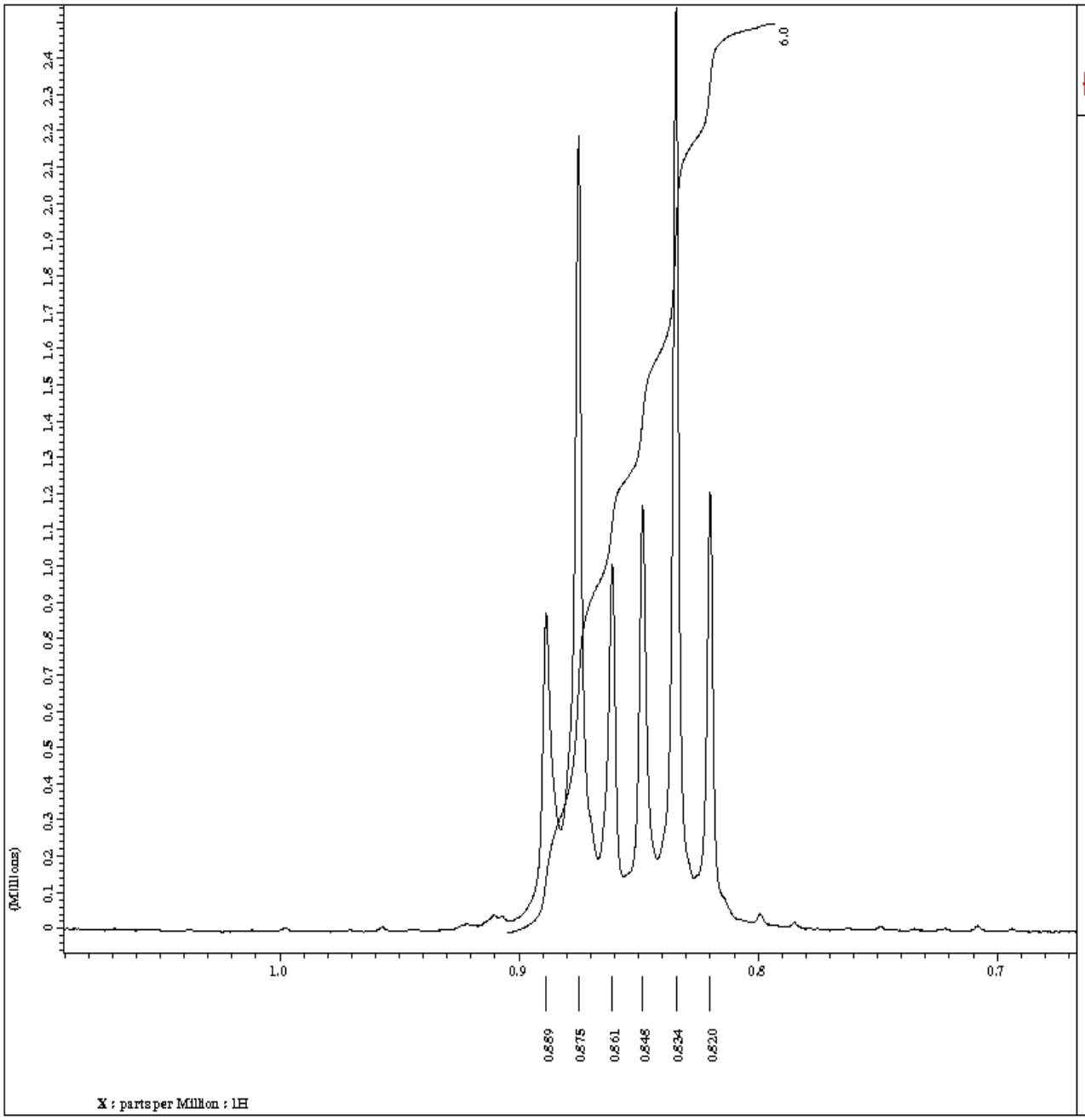

59



JEOL

Filename	= H-T-Di-F-Hep--5.jdf
Author	= delta
Experiment	= single_pulse.exp
Sample_id	= S#426198
Solvent	= CHLOROFORM-D
Creation_time	= 29-JUN-2007 15:47:47
Revision_time	= 10-DEC-2008 17:44:01
Current_time	= 10-DEC-2008 17:48:35
Comment	= Single Pulse Experime
Data_format	= 1D COMPLEX
Dim_size	= 65536
Dim_title	= 1H
Dim_units	= [ppm]
Dimensions	= X
Site	= Eclipse+ 500
Spectrometer	= DELTA_NMR
Field_strength	= 11.7473579[T] (500[MH
X_acq_duration	= 0.7293952[s]
X_domain	= 1H
X_freq	= 500.15991521[MHz]
X_offset	= 5[ppm]
X_points	= 65536
X_prescans	= 0
X_resolution	= 0.11455547[Hz]
X_sweep	= 7.50750751[kHz]
Clipped	= FALSE
Mod_return	= 1
Scans	= 20
Total_scans	= 20
X_90_width	= 10.5[us]
X_acq_time	= 0.7293952[s]
X_angle	= 45[deg]
X_pulse	= 9.25[us]
Initial_wait	= 1[s]
Phase_preset	= 3[us]
Recvr_gain	= 20
Relaxation_delay	= 30[s]
Temp_get	= 24.4[dC]
Unblank_time	= 2[us]

59



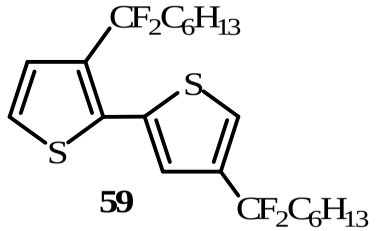
JEOL

```
Filename          = H-T-Di-F-Hep--5.jdf
Author            = delta
Experiment        = single_pulse.exp
Sample_id         = S#426198
Solvent           = CHLOROFORM-D
Creation_time     = 29-JUN-2007 15:47:47
Revision_time     = 10-DEC-2008 17:44:01
Current_time      = 10-DEC-2008 17:48:58

Comment           = Single Pulse Experime
Data_format       = 1D COMPLEX
Dim_size          = 65536
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 0.7299352[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 5[ppm]
X_points          = 65536
X_prescans        = 0
X_resolution      = 0.11455547[Hz]
X_sweep           = 7.50750751[kHz]
Clipped           = FALSE
Mod_return        = 1
Scans             = 20
Total_scans       = 20

X_90_width        = 10.5[us]
X_acq_time        = 0.7299352[s]
X_angle           = 45[deg]
X_pulse           = 9.25[us]
Initial_wait      = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 20
Relaxation_delay  = 30[s]
Temp_get          = 24.4[dC]
Unblank_time      = 2[us]
```



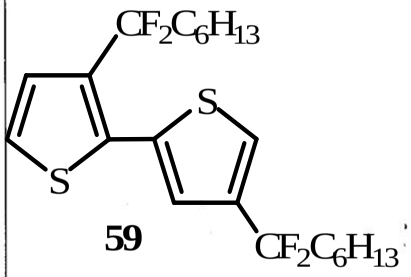
59

```
Filename          = H-T-Di-F-Hex-Th-4.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#836861
Solvent           = CHLOROFORM-D
Creation_time     =  3-JUL-2007 12:54:12
Revision_time     =  3-JUL-2007 11:35:43
Current_time      =  3-JUL-2007 11:35:58

Content           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 65536
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 2.0840448[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 65536
X_prescans        = 4
X_resolution      = 0.47983613[Hz]
X_sweep           = 31.44654088[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 7000
Total_scans       = 7000

X_90_width        = 14.2[us]
X_acq_time        = 2.0840448[s]
X_angle           = 30[deg]
X_pulse           = 4.73333333[us]
Initial_wait      = 1[s]
Noe_time          = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 29
Relaxation_delay  = 2[s]
Temp_get          = 26.8[dC]
Unblank_time      = 2[us]
```



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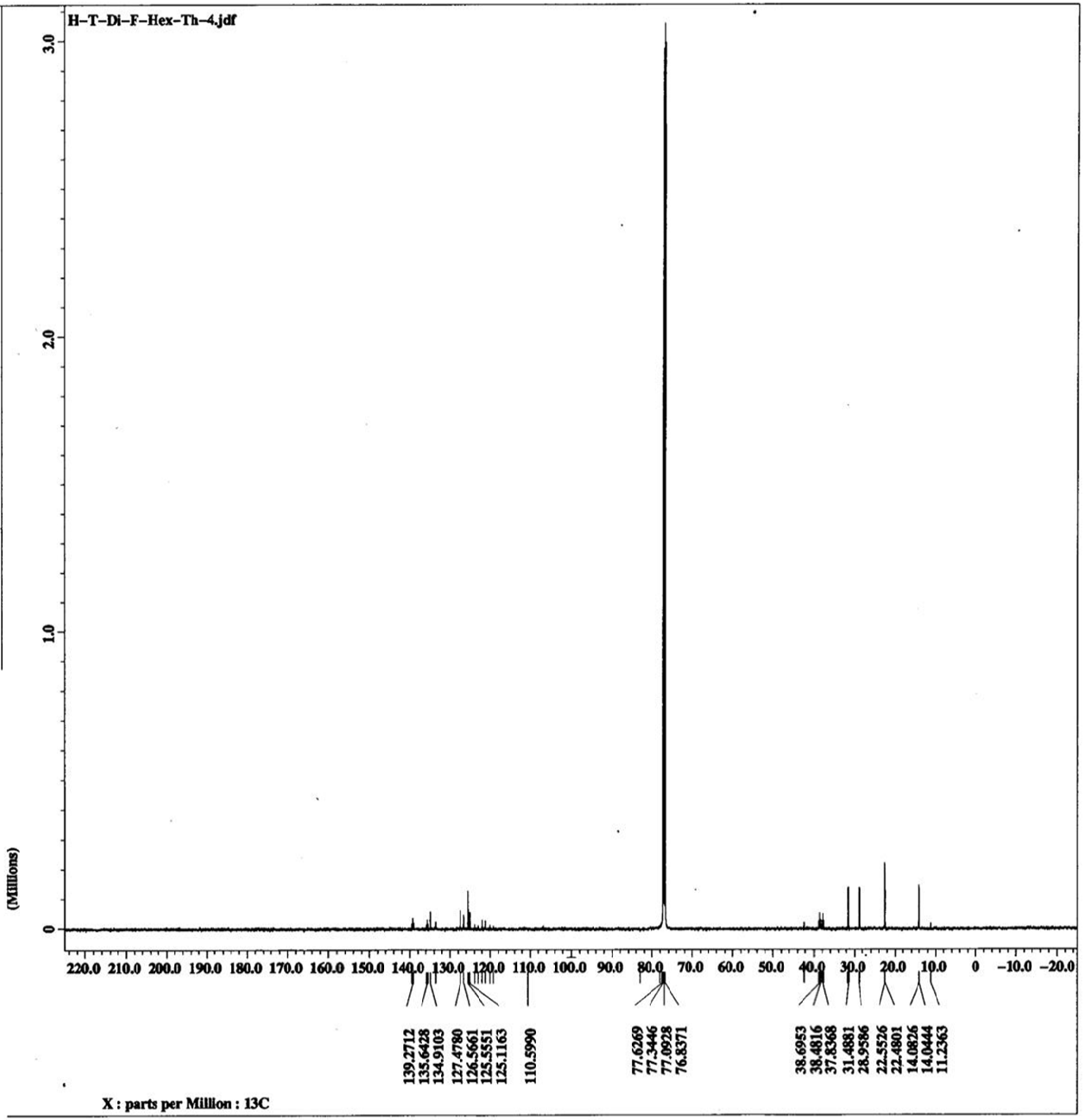
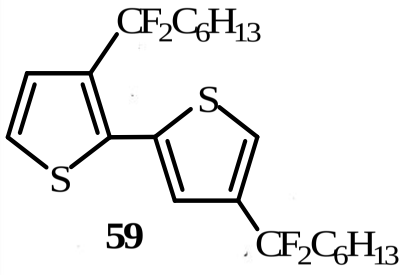


H-T-Di-F-Hex-Th-4.jdf
Filename = H-T-Di-F-Hex-Th-4.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = S#836861
Solvent = CHLOROFORM-D
Creation_time = 3-JUL-2007 12:54:12
Revision_time = 3-JUL-2007 11:35:43
Current_time = 3-JUL-2007 11:35:50
Content = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 65536
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.0840448[s]
X_domain = 13C
X_freq = 125.76529768[MHz]
X_offset = 100[ppm]
X_points = 65536
X_prescans = 4
X_resolution = 0.47983613[Hz]
X_sweep = 31.44654088[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 7000
Total_scans = 7000
X_90_width = 14.2[us]
X_acq_time = 2.0840448[s]
X_angle = 30[deg]
X_pulse = 4.73333333[us]
Initial_wait = 1[s]
Noe_time = 1[s]
Phase_preset = 3[us]
Recvr_gain = 29
Relaxation_delay = 2[s]
Temp_get = 26.8[dC]
Unblank_time = 2[us]
(Thousands)
60.0
50.0
40.0
30.0
20.0
10.0
0
139.5116
139.2712
139.0346
138.0
137.0
136.0
135.8755
135.6428
135.4139
135.0
134.9103
134.0
133.6321
133.0
X : parts per Million : 13C
59

Filename	= H-T-Di-F-Hex-Th-4.jdf
Author	= delta
Experiment	= single_pulse_dec
Sample_id	= S#836861
Solvent	= CHLOROFORM-D
Creation_time	= 3-JUL-2007 12:54:12
Revision_time	= 3-JUL-2007 11:34:25
Current_time	= 3-JUL-2007 11:34:29
Content	= single pulse decouple
Data_format	= 1D COMPLEX
Dim_size	= 65536
Dim_title	= 13C
Dim_units	= [ppm]
Dimensions	= X
Site	= Eclipse+ 500
Spectrometer	= DELTA_NMR
Field_strength	= 11.7473579[T] (500[MH
X_acq_duration	= 2.0840448[s]
X_domain	= 13C
X_freq	= 125.76529768[MHz]
X_offset	= 100[ppm]
X_points	= 65536
X_prescans	= 4
X_resolution	= 0.47983613[Hz]
X_sweep	= 31.44654088[kHz]
Irr_domain	= 1H
Irr_freq	= 500.15991521[MHz]
Irr_offset	= 5[ppm]
Clipped	= FALSE
Mod_return	= 1
Scans	= 7000
Total_scans	= 7000
X_90_width	= 14.2[us]
X_acq_time	= 2.0840448[s]
X_angle	= 30[deg]
X_pulse	= 4.73333333[us]
Initial_wait	= 1[s]
Noe_time	= 1[s]
Phase_preset	= 3[us]
Recvr_gain	= 29
Relaxation_delay	= 2[s]
Temp_get	= 26.8[dC]
Unblank_time	= 2[us]



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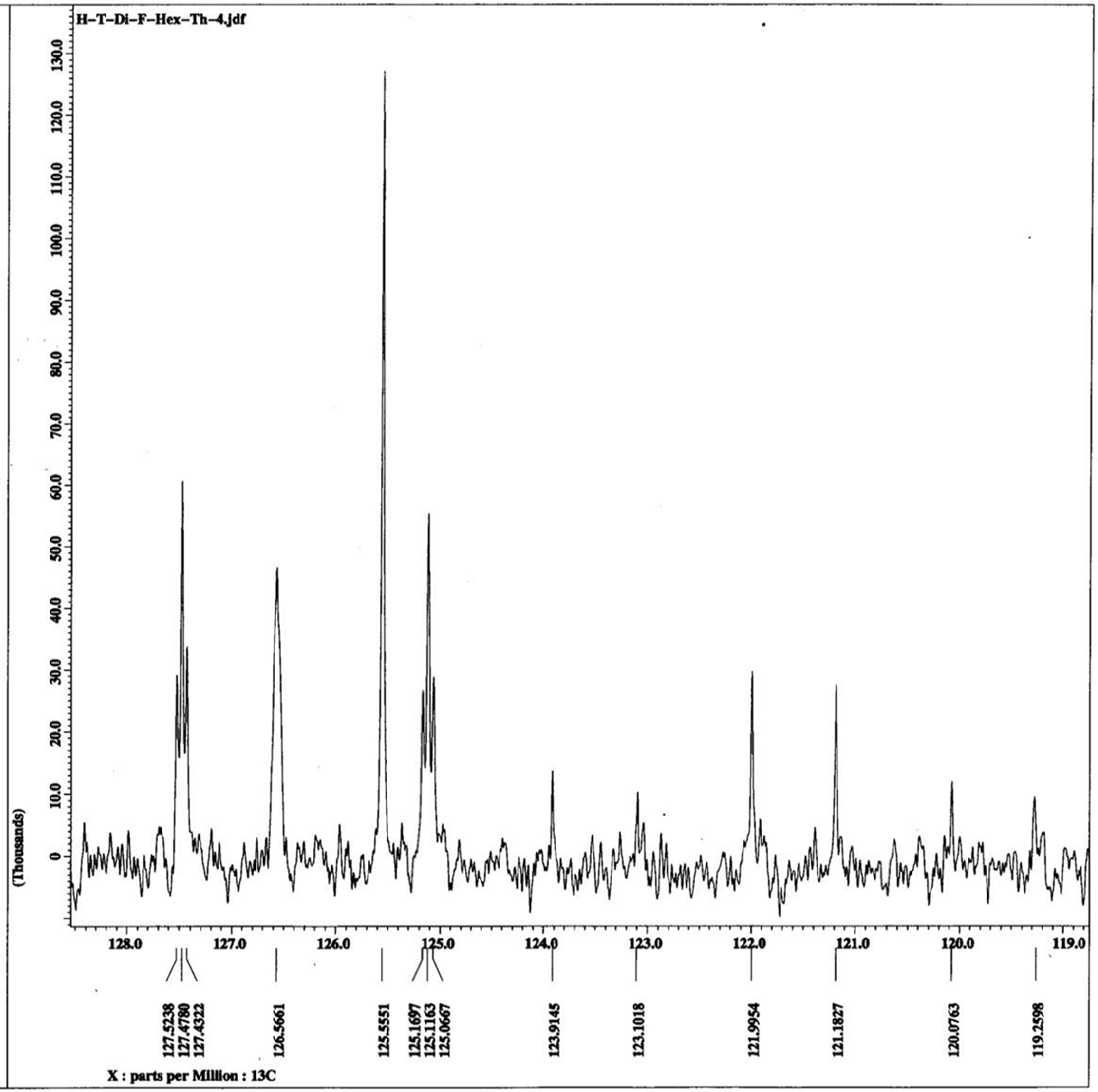
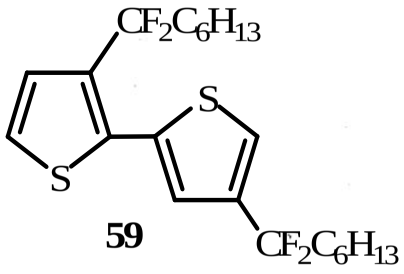


Filename	= H-T-Di-F-Hex-Th-4.jdf
Author	= delta
Experiment	= single_pulse_dec
Sample_id	= S#836861
Solvent	= CHLOROFORM-D
Creation_time	= 3-JUL-2007 12:54:12
Revision_time	= 3-JUL-2007 11:32:47
Current_time	= 3-JUL-2007 11:32:51
Content	= single pulse decouple
Data_format	= 1D COMPLEX
Dim_size	= 65536
Dim_title	= 13C
Dim_units	= [ppm]
Dimensions	= X
Site	= Eclipse+ 500
Spectrometer	= DELTA_NMR
Field_strength	= 11.7473579[T] (500[MH
X_acq_duration	= 2.0840448[s]
X_domain	= 13C
X_freq	= 125.76529768[MHz]
X_offset	= 100[ppm]
X_points	= 65536
X_prescans	= 4
X_resolution	= 0.47983613[Hz]
X_sweep	= 31.44654088[kHz]
Irr_domain	= 1H
Irr_freq	= 500.15991521[MHz]
Irr_offset	= 5[ppm]
Clipped	= FALSE
Mod_return	= 1
Scans	= 7000
Total_scans	= 7000
X_90_width	= 14.2[us]
X_acq_time	= 2.0840448[s]
X_angle	= 30[deg]
X_pulse	= 4.73333333[us]
Initial_wait	= 1[s]
Noe_time	= 1[s]
Phase_preset	= 3[us]
Recvr_gain	= 29
Relaxation_delay	= 2[s]
Temp_get	= 26.8[dC]
Unblank_time	= 2[us]



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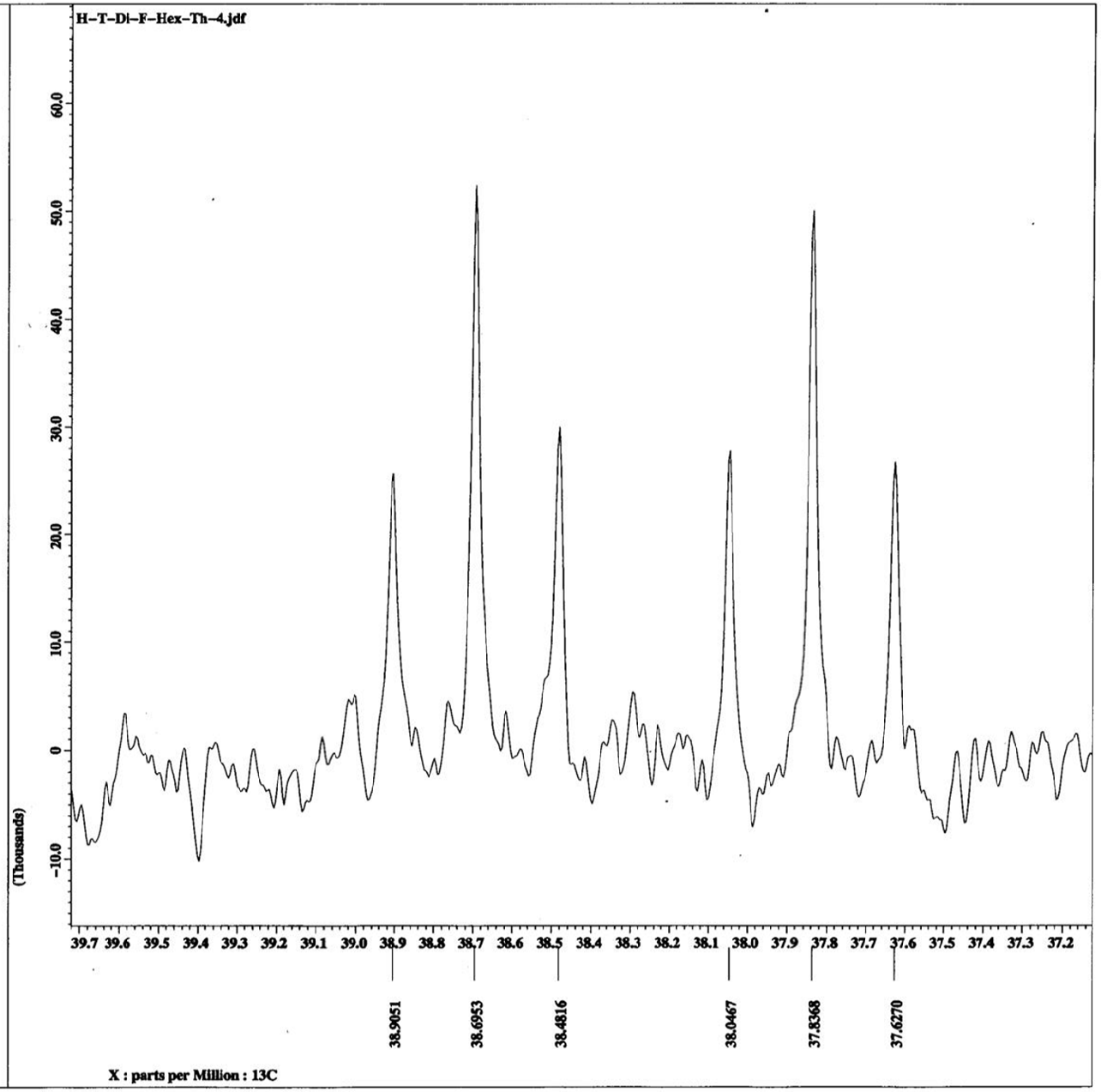
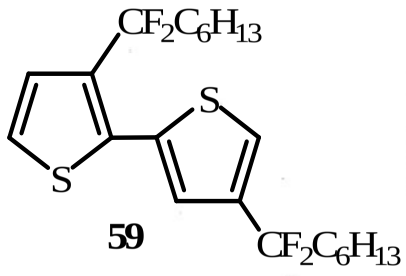
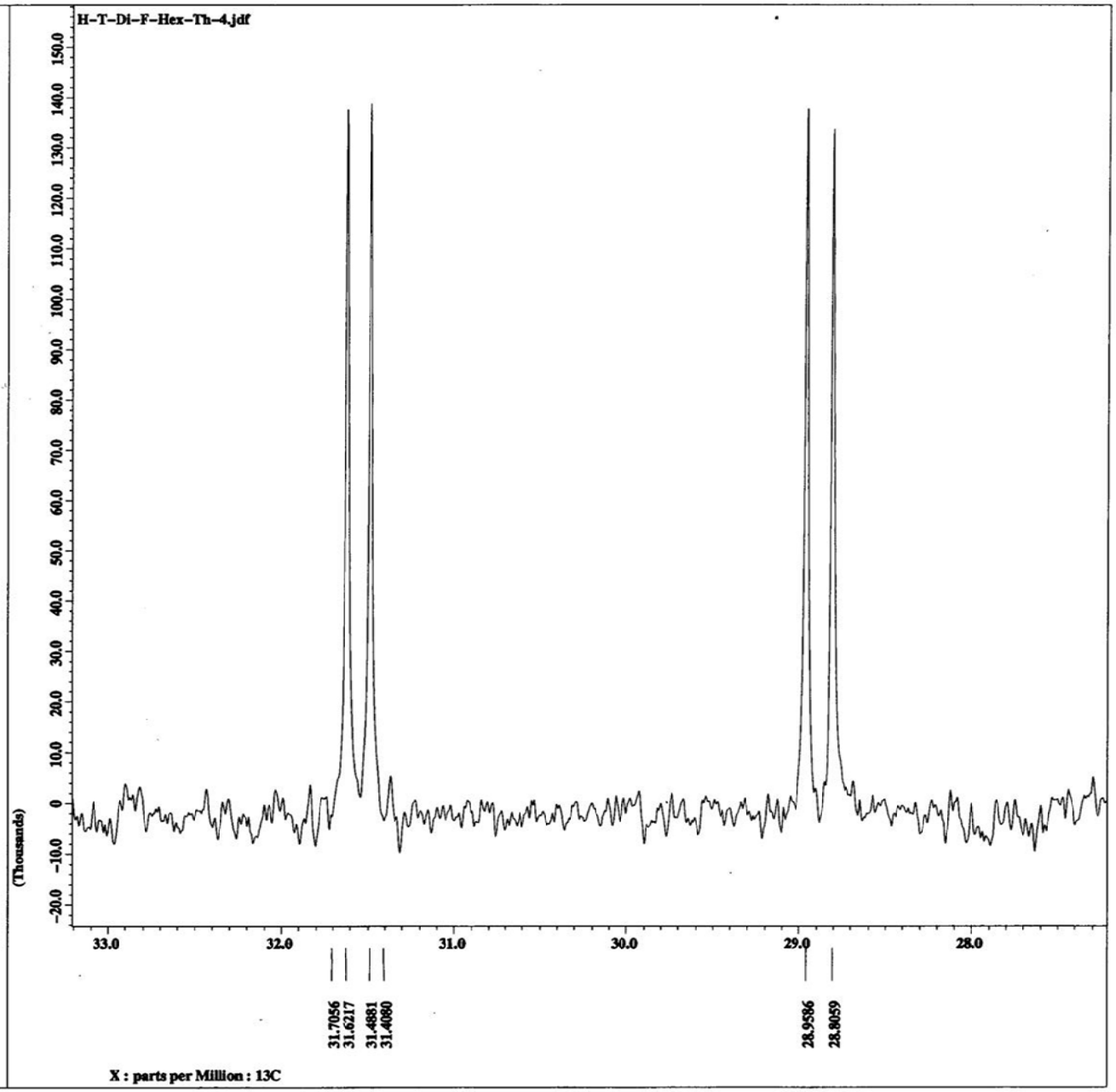


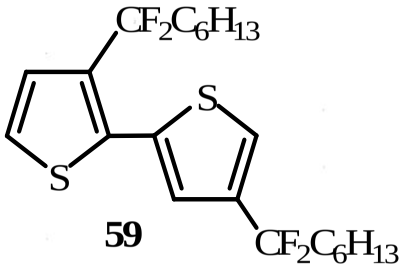
Filename	= H-T-Di-F-Hex-Th-4.jdf
Author	= delta
Experiment	= single_pulse_dec
Sample_id	= S#836861
Solvent	= CHLOROFORM-D
Creation_time	= 3-JUL-2007 12:54:12
Revision_time	= 3-JUL-2007 11:31:57
Current_time	= 3-JUL-2007 11:32:27
Content	= single pulse decouple
Data_format	= 1D COMPLEX
Dim_size	= 65536
Dim_title	= 13C
Dim_units	= [ppm]
Dimensions	= X
Site	= Eclipse+ 500
Spectrometer	= DELTA_NMR
Field_strength	= 11.7473579[T] (500[MH
X_acq_duration	= 2.0840448[s]
X_domain	= 13C
X_freq	= 125.76529768[MHz]
X_offset	= 100[ppm]
X_points	= 65536
X_prescans	= 4
X_resolution	= 0.47983613[Hz]
X_sweep	= 31.44654088[kHz]
Irr_domain	= 1H
Irr_freq	= 500.15991521[MHz]
Irr_offset	= 5[ppm]
Clipped	= FALSE
Mod_return	= 1
Scans	= 7000
Total_scans	= 7000
X_90_width	= 14.2[us]
X_acq_time	= 2.0840448[s]
X_angle	= 30[deg]
X_pulse	= 4.73333333[us]
Initial_wait	= 1[s]
Noe_time	= 1[s]
Phase_preset	= 3[us]
Recvr_gain	= 29
Relaxation_delay	= 2[s]
Temp_get	= 26.8[dC]
Unblank_time	= 2[us]



59



Filename	= H-T-Di-F-Hex-Th-4.jdf
Author	= delta
Experiment	= single_pulse_dec
Sample_id	= S@836861
Solvent	= CHLOROFORM-D
Creation_time	= 3-JUL-2007 12:54:12
Revision_time	= 3-JUL-2007 11:31:57
Current_time	= 3-JUL-2007 11:32:13
Content	= single pulse decouple
Data_format	= 1D COMPLEX
Dim_size	= 65536
Dim_title	= 13C
Dim_units	= [ppm]
Dimensions	= X
Site	= Eclipse+ 500
Spectrometer	= DELTA_NMR
Field_strength	= 11.7473579[T] (500[MH
X_acq_duration	= 2.0840448[s]
X_domain	= 13C
X_freq	= 125.76529768[MHz]
X_offset	= 100[ppm]
X_points	= 65536
X_prescans	= 4
X_resolution	= 0.47983613[Hz]
X_sweep	= 31.44654088[kHz]
Irr_domain	= 1H
Irr_freq	= 500.15991521[MHz]
Irr_offset	= 5[ppm]
Clipped	= FALSE
Mod_return	= 1
Scans	= 7000
Total_scans	= 7000
X_90_width	= 14.2[us]
X_acq_time	= 2.0840448[s]
X_angle	= 30[deg]
X_pulse	= 4.73333333[us]
Initial_wait	= 1[s]
Noe_time	= 1[s]
Phase_preset	= 3[us]
Recvr_gain	= 29
Relaxation_delay	= 2[s]
Temp_get	= 26.8[dC]
Unblank_time	= 2[us]



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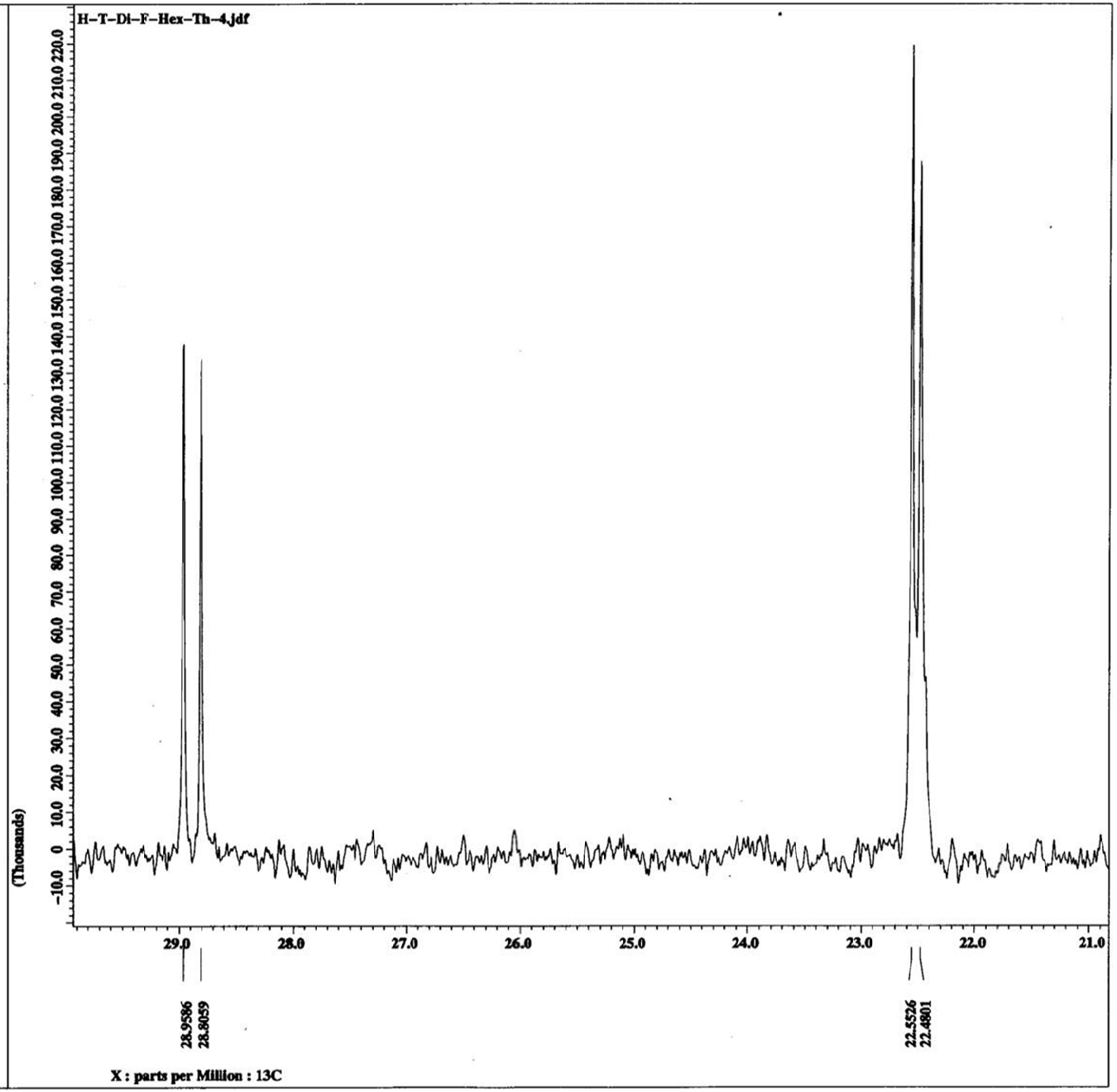
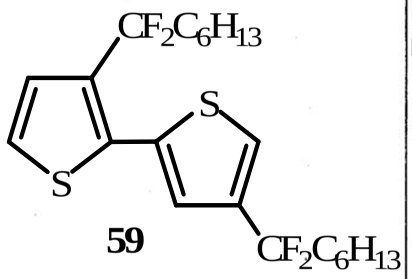
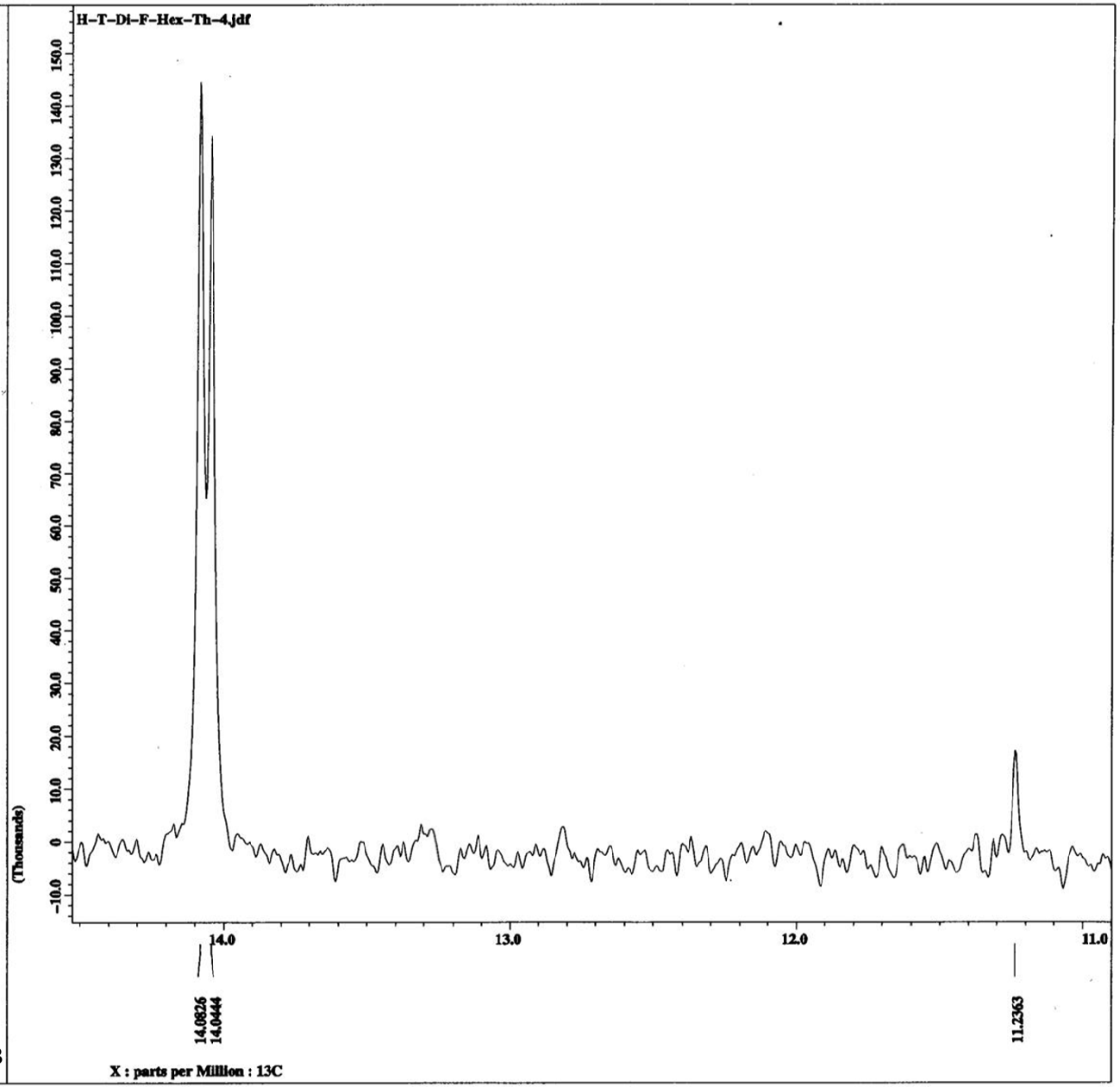


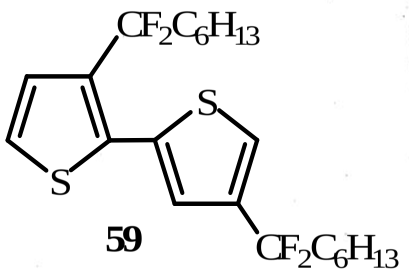
Filename	= H-T-Di-F-Hex-Th-4.jdf
Author	= delta
Experiment	= single_pulse_dec
Sample_id	= s#836861
Solvent	= CHLOROFORM-D
Creation_time	= 3-JUL-2007 12:54:12
Revision_time	= 3-JUL-2007 11:31:16
Current_time	= 3-JUL-2007 11:31:27
Content	= single pulse decouple
Data_format	= 1D COMPLEX
Dim_size	= 65536
Dim_title	= 13C
Dim_units	= [ppm]
Dimensions	= X
Site	= Eclipse+ 500
Spectrometer	= DELTA_NMR
Field_strength	= 11.7473579[T] (500[MH
X_acq_duration	= 2.0840448[s]
X_domain	= 13C
X_freq	= 125.76529768[MHz]
X_offset	= 100[ppm]
X_points	= 65536
X_prescans	= 4
X_resolution	= 0.47983613[Hz]
X_sweep	= 31.44654088[kHz]
Irr_domain	= 1H
Irr_freq	= 500.15991521[MHz]
Irr_offset	= 5[ppm]
Clipped	= FALSE
Mod_return	= 1
Scans	= 7000
Total_scans	= 7000
X_90_width	= 14.2[us]
X_acq_time	= 2.0840448[s]
X_angle	= 30[deg]
X_pulse	= 4.73333333[us]
Initial_wait	= 1[s]
Noe_time	= 1[s]
Phase_preset	= 3[us]
Recvr_gain	= 29
Relaxation_delay	= 2[s]
Temp_get	= 26.8[dC]
Unblank_time	= 2[us]



59



Filename	= H-T-Hex-di-F-Th-7.jdf
Author	= delta
Experiment	= single_pulse.ex2
Sample_id	= S@583227
Solvent	= CHLOROFORM-D
Creation_time	= 8-JUL-2007 16:49:18
Revision_time	= 8-JUL-2007 16:29:11
Current_time	= 8-JUL-2007 16:29:27
Content	= single_pulse
Data_format	= 1D COMPLEX
Dim_size	= 1572840
Dim_title	= 19F
Dim_units	= [ppm]
Dimensions	= X
Site	= ECX 300
Spectrometer	= DELTA2_NMR
Field_strength	= 7.0586013[T] (300[MHz
X_acq_duration	= 1.1534336[s]
X_domain	= 19F
X_freq	= 282.78036857[MHz]
X_offset	= -60[ppm]
X_points	= 65536
X_prescans	= 0
X_resolution	= 0.86697665[Hz]
X_sweep	= 56.81818182[kHz]
Irr_domain	= 19F
Irr_freq	= 282.78036857[MHz]
Irr_offset	= 5[ppm]
Tri_domain	= 19F
Tri_freq	= 282.78036857[MHz]
Tri_offset	= 5[ppm]
Clipped	= TRUE
Mod_return	= 0
Scans	= 20
Total_scans	= 20
X_90_width	= 10[us]
X_acq_time	= 1.1534336[s]
X_angle	= 45[deg]
X_atn	= 4[dB]
X_pulse	= 5[us]
Irr_mode	= Off
Tri_mode	= Off
Dante_presat	= FALSE
Initial_wait	= 1[s]
Recvr_gain	= 50
Relaxation_delay	= 30[s]
Repetition_time	= 31.1534336[s]
Temp_get	= 22.8[dC]



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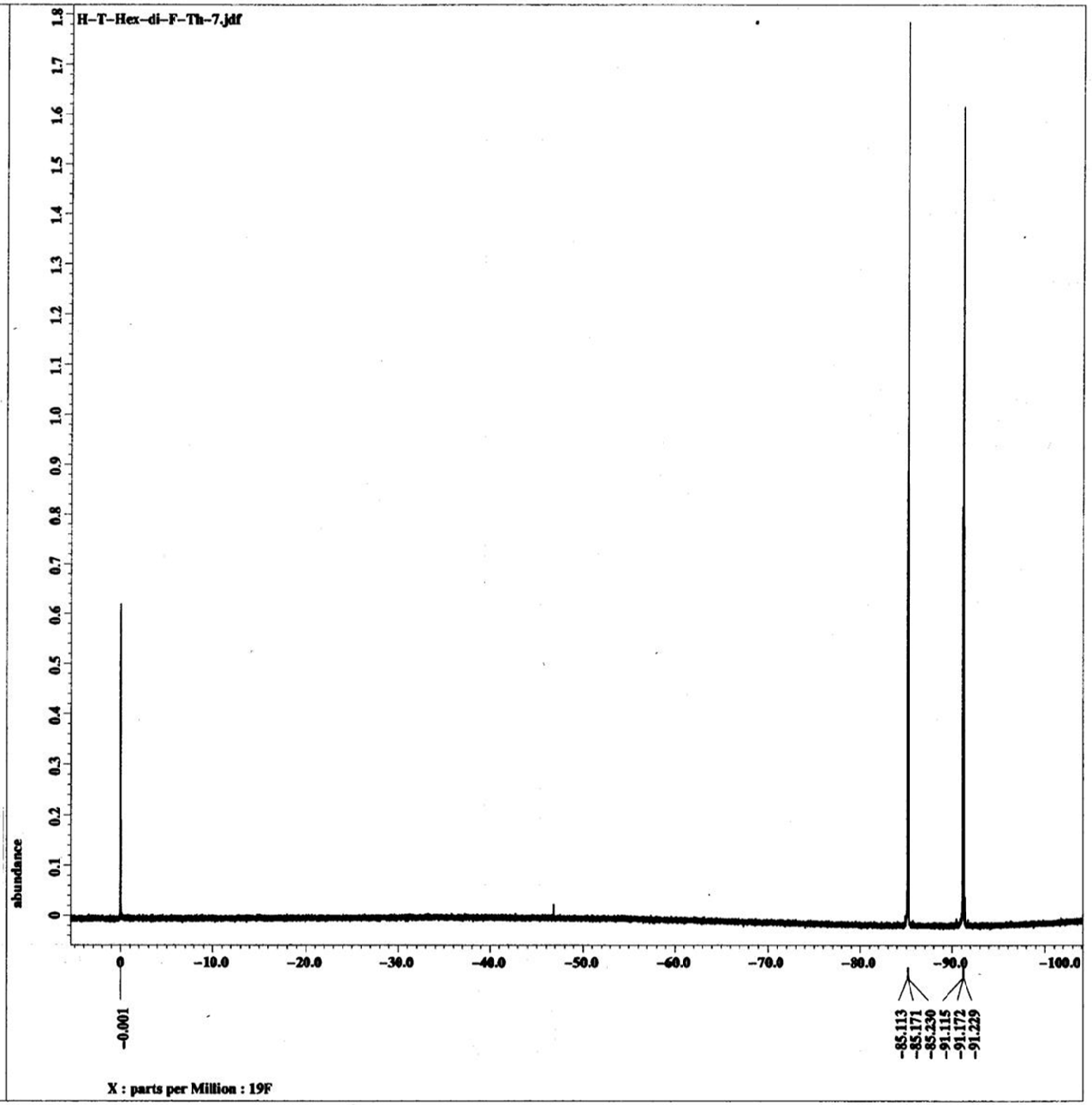
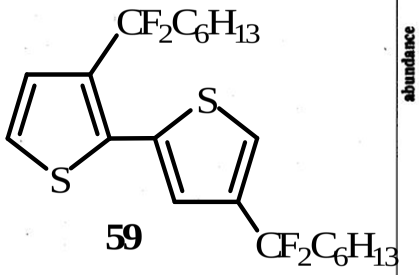


Filename	= H-T-Hex-di-F-Th-7.jdf
Author	= delta
Experiment	= single_pulse.ex2
Sample_id	= S@583227
Solvent	= CHLOROFORM-D
Creation_time	= 8-JUL-2007 16:49:18
Revision_time	= 8-JUL-2007 16:30:15
Current_time	= 8-JUL-2007 16:30:19
Content	= single_pulse
Data_format	= 1D COMPLEX
Dim_size	= 1572840
Dim_title	= 19F
Dim_units	= [ppm]
Dimensions	= X
Site	= ECX 300
Spectrometer	= DELTA2_NMR
Field_strength	= 7.0586013[T] (300[MHz
X_acq_duration	= 1.1534336[s]
X_domain	= 19F
X_freq	= 282.78036857[MHz]
X_offset	= -60[ppm]
X_points	= 65536
X_prescans	= 0
X_resolution	= 0.86697665[Hz]
X_sweep	= 56.81818182[kHz]
Irr_domain	= 19F
Irr_freq	= 282.78036857[MHz]
Irr_offset	= 5[ppm]
Tri_domain	= 19F
Tri_freq	= 282.78036857[MHz]
Tri_offset	= 5[ppm]
Clipped	= TRUE
Mod_return	= 0
Scans	= 20
Total_scans	= 20
X_90_width	= 10[us]
X_acq_time	= 1.1534336[s]
X_angle	= 45[deg]
X_atn	= 4[dB]
X_pulse	= 5[us]
Irr_mode	= Off
Tri_mode	= Off
Dante_presat	= FALSE
Initial_wait	= 1[s]
Recvr_gain	= 50
Relaxation_delay	= 30[s]
Repetition_time	= 31.1534336[s]
Temp_get	= 22.8[dC]



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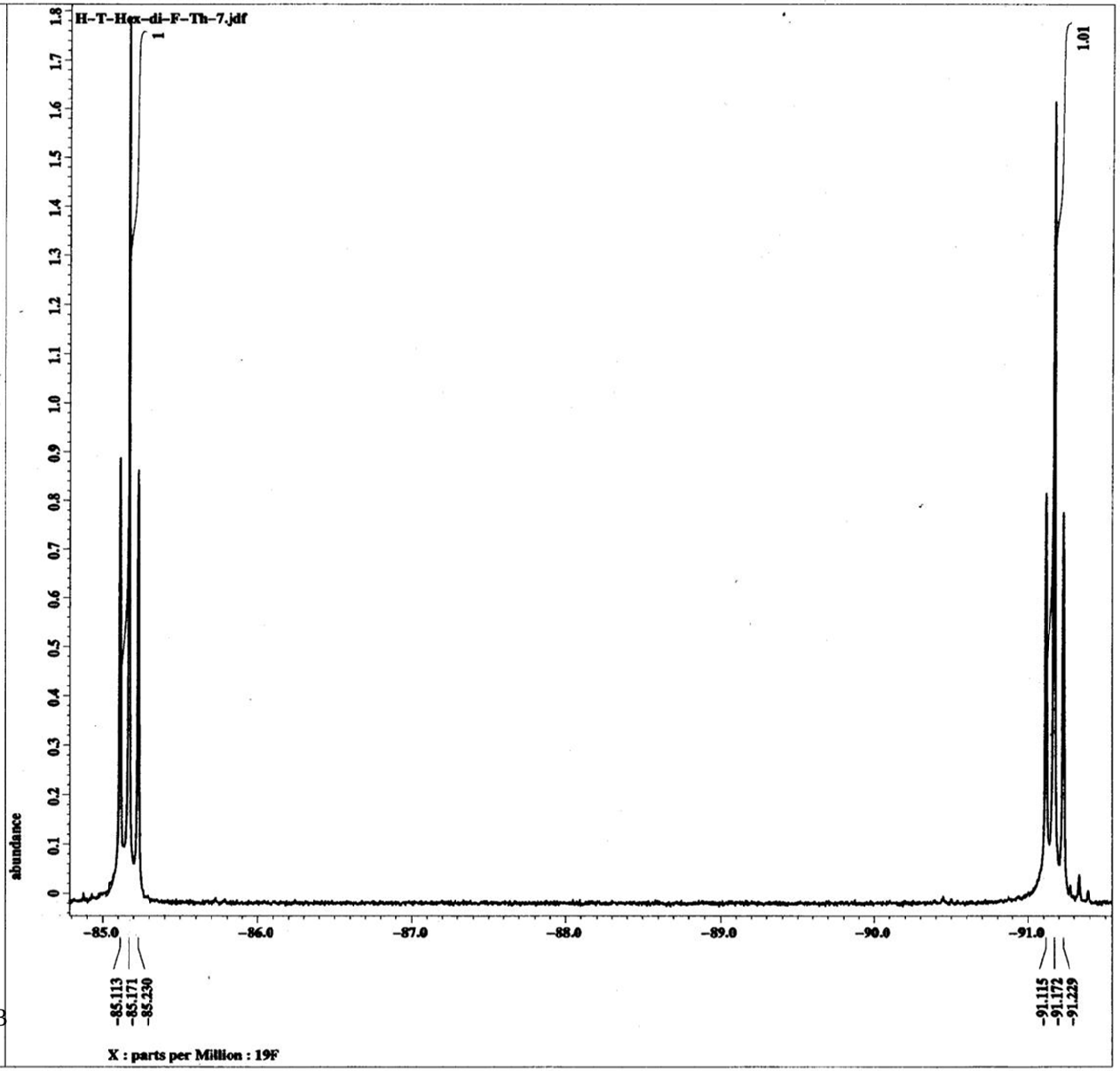

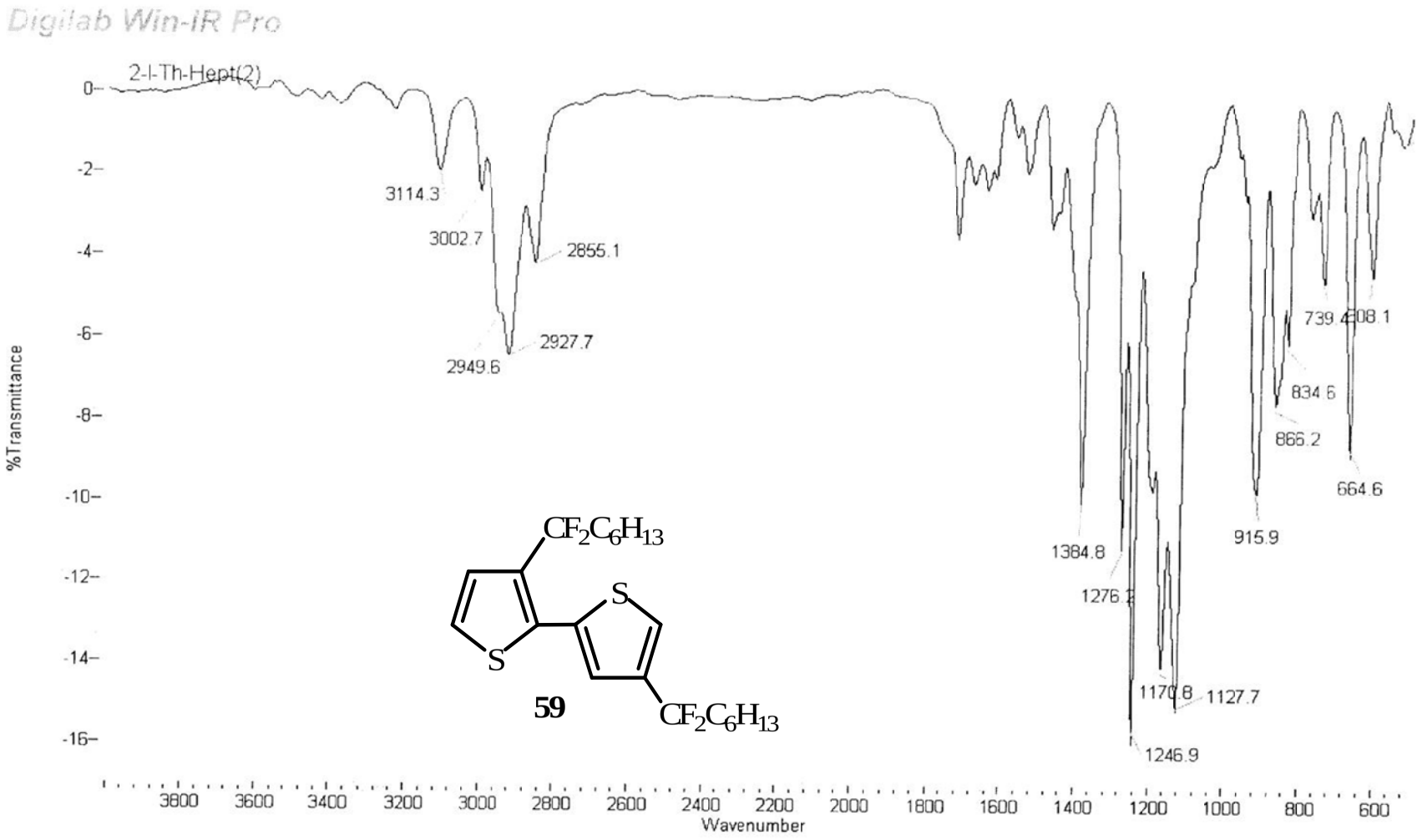
Digilab Win-IR Pro
2-I-Th-Hept(2)
%Transmittance
0
-2
-4
-6
-8
-10
-12
-14
-16
3114.3
3002.7
2855.1
2949.6
2927.7
1384.8
1276.2
1170.8
1127.7
1246.9
915.9
834.6
866.2
739.4
708.1
664.6
$CF_2C_6H_{13}$
S
S
$CF_2C_6H_{13}$
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
Wavenumber

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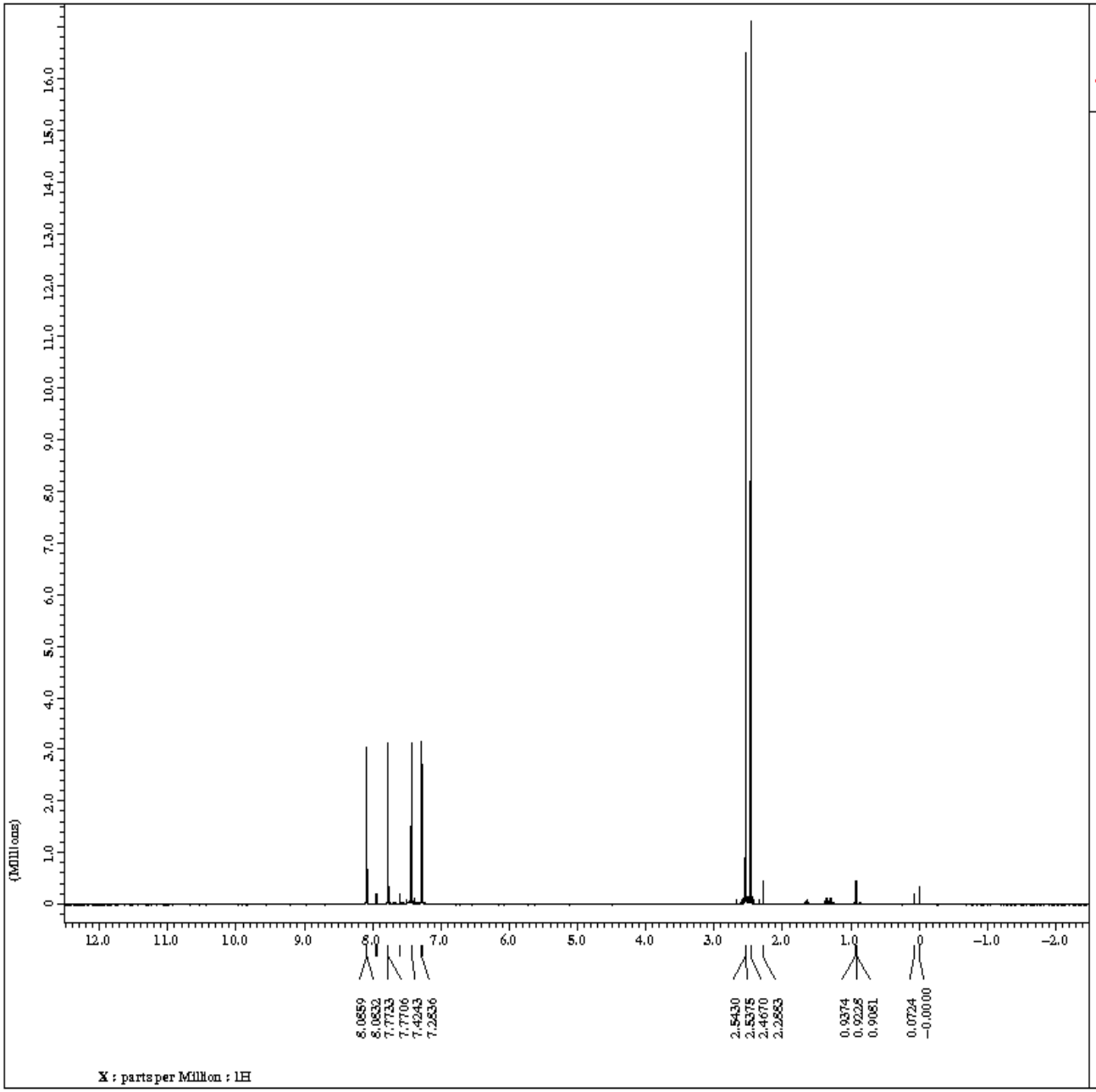
APPENDIX 11

^{1}H, ^{13}C NMR and IR spectra of 3,4'-diethanoyl -2,2'-bithiophene (**88**)



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Author = delta
Experiment = single_pulse.exp
Sample_id = S#673304
Solvent = CHLOROFORM-D
Creation_time = 14-OCT-2008 02:15:40
Revision_time = 3-NOV-2008 22:56:51
Current_time = 3-NOV-2008 22:57:45

Comment = Single Pulse Experime
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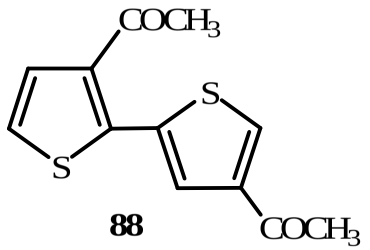
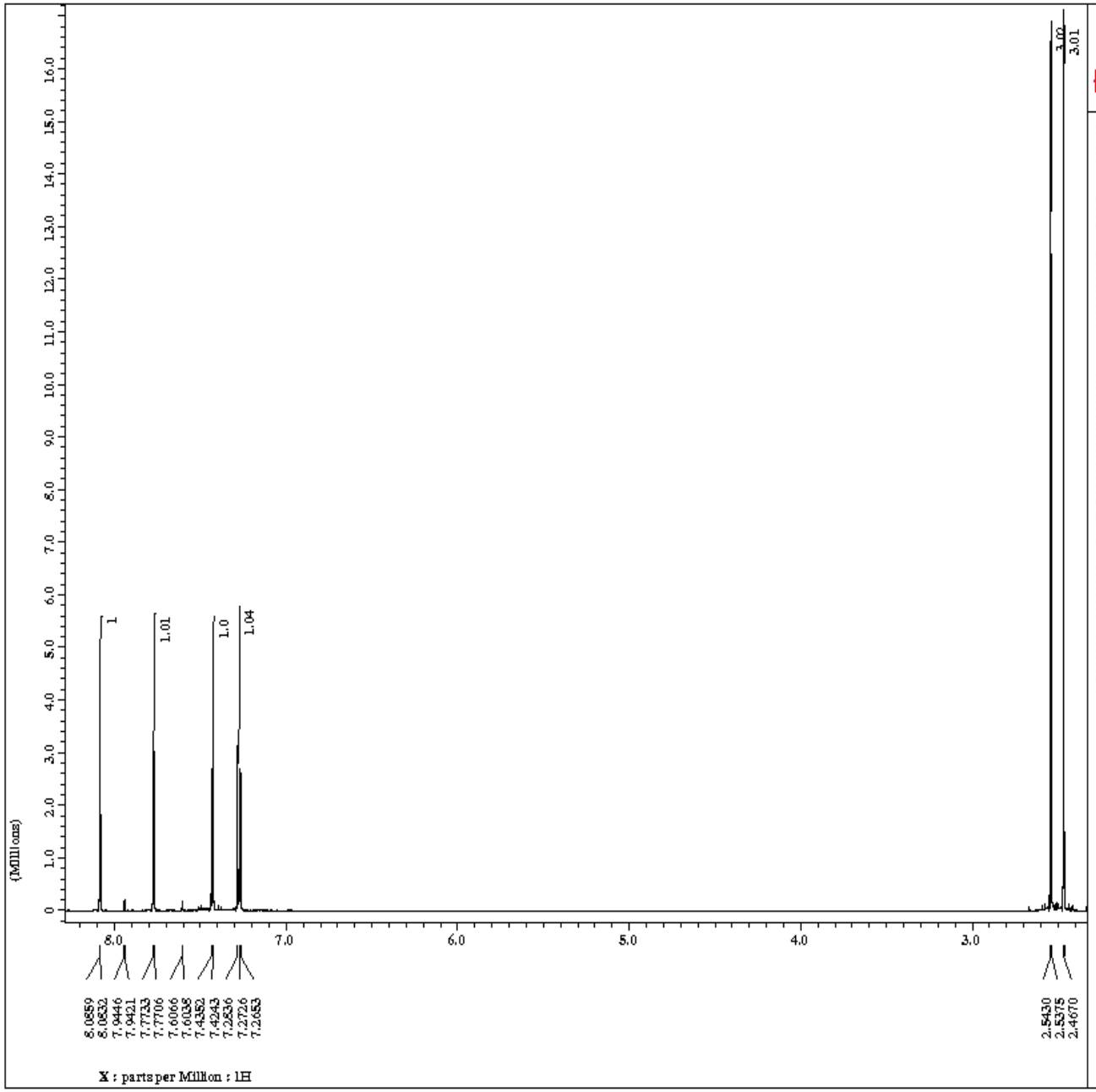
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR

Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 0.7293952[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 65536
X_prescans = 0
X_resolution = 0.11455547[Hz]
X_sweep = 7.50750751[kHz]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8

X_90_width = 10.5[us]
X_acq_time = 0.7293952[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 20
Relaxation_delay = 14[s]
Temp_get = 26.6[dC]
Unblank_time = 2[us]



88



JEOL

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Filename          = H-T-ethyl-ketone-7.jd
Author            = delta
Experiment        = single_pulse.exp
Sample_id         = S#673304
Solvent           = CHLOROFORM-D
Creation_time     = 14-OCT-2008 02:15:40
Revision_time     =  3-NOV-2008 23:04:38
Current_time      =  3-NOV-2008 23:04:59

Comment           = Single Pulse Experime
Data_format       = 1D COMPLEX
Dim_size          = 65536
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 0.7293952[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 5[ppm]
X_points          = 65536
X_prescans        = 0
X_resolution      = 0.11455547[Hz]
X_sweep           = 7.50750751[kHz]
Clipped           = FALSE
Mod_return        = 1
Scans             = 8
Total_scans       = 8

X_90_width        = 10.5[us]
X_acq_time        = 0.7293952[s]
X_angle           = 45[deg]
X_pulse           = 9.25[us]
Initial_wait      = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 20
Relaxation_delay  = 14[s]
Temp_get          = 26.6[dC]
Unblank_time      = 2[us]
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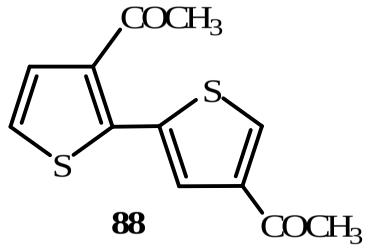

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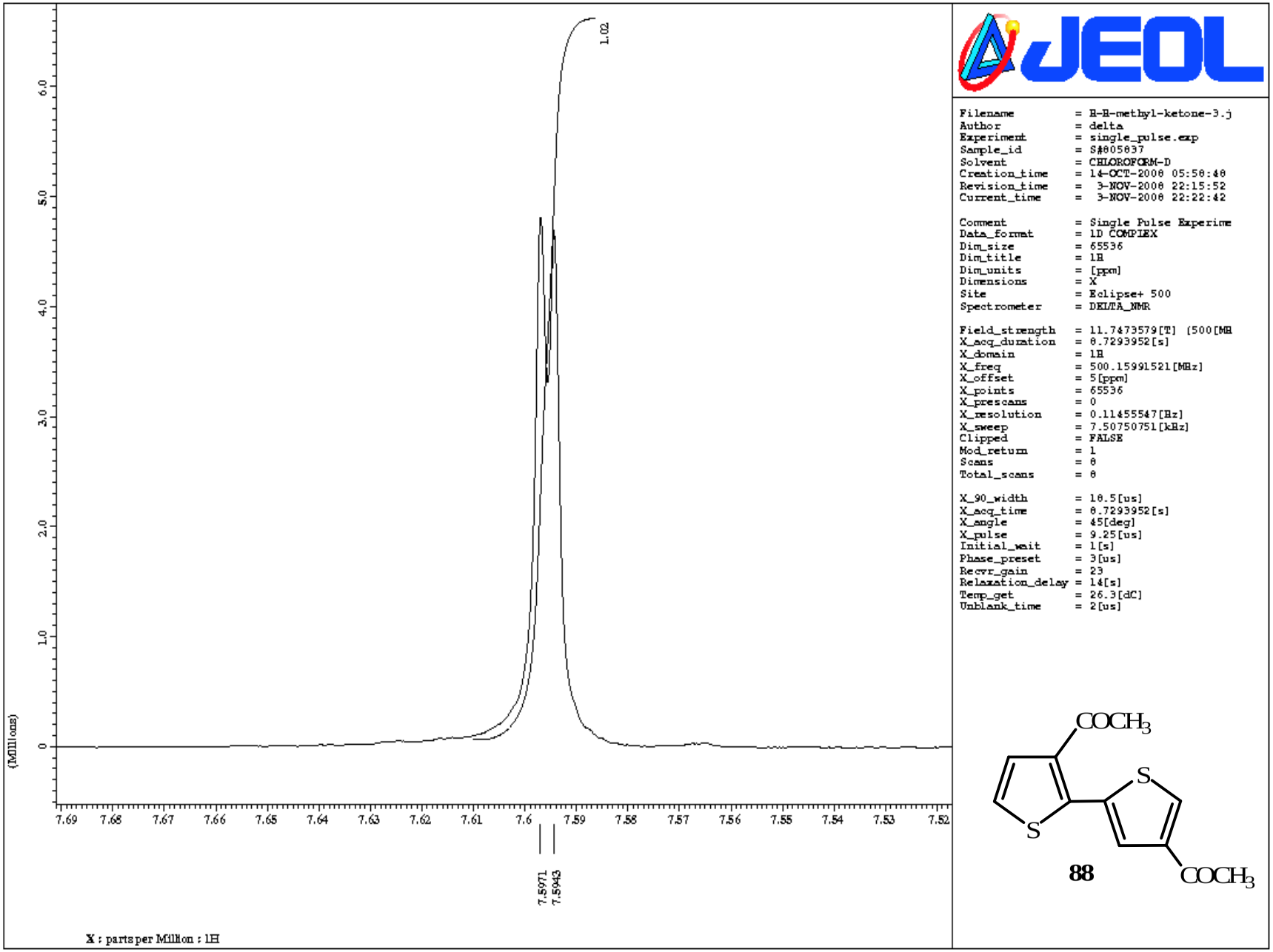


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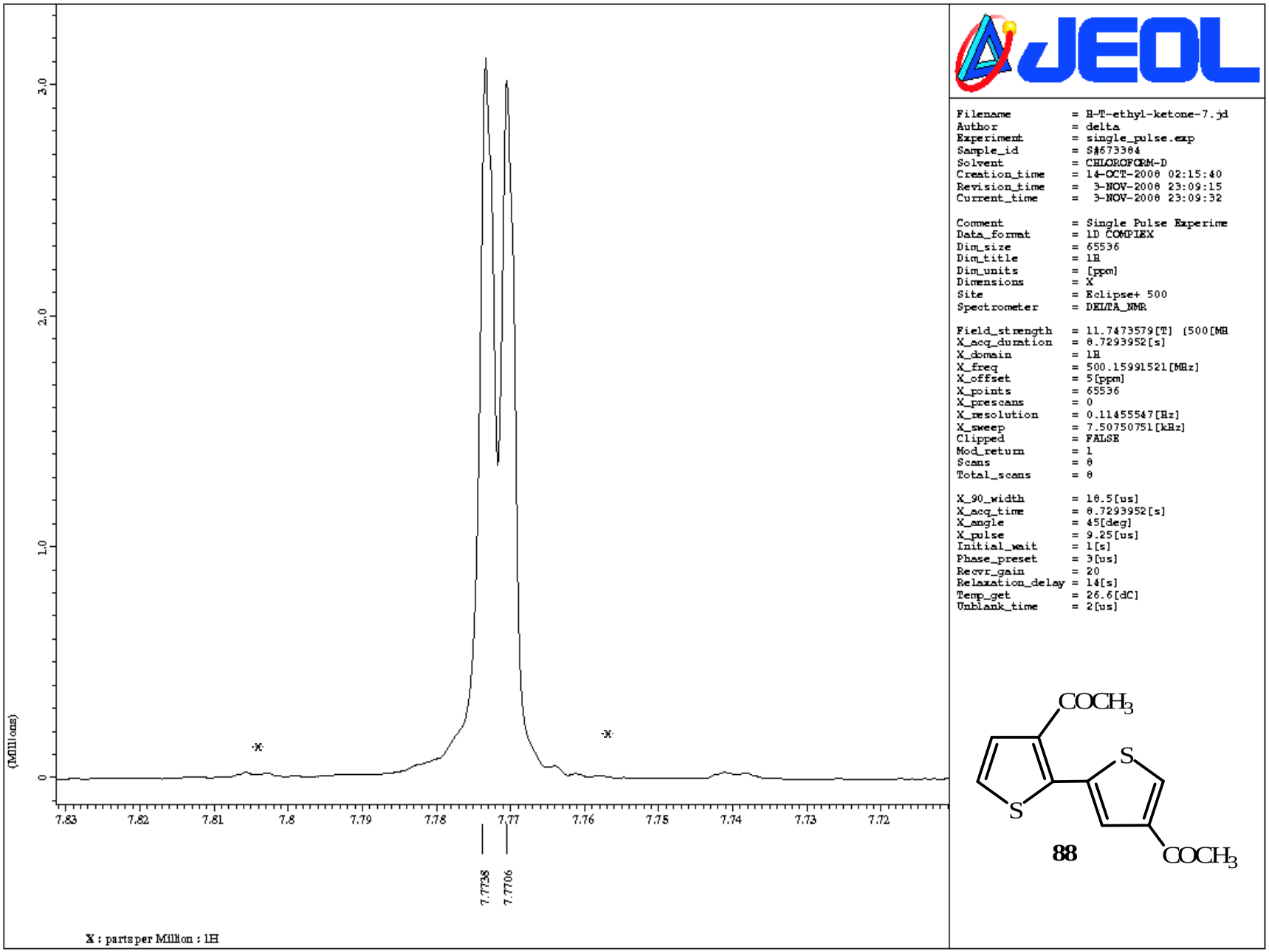
Filename          = H-H-methyl-ketone-3.j
Author            = delta
Experiment        = single_pulse.exp
Sample_id         = S#005037
Solvent           = CHLOROFORM-D
Creation_time     = 14-OCT-2008 05:58:48
Revision_time     =  3-NOV-2008 22:15:52
Current_time      =  3-NOV-2008 22:22:42

Comment           = Single Pulse Experime
Data_format       = 1D COMPLEX
Dim_size          = 65536
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 0.7293952[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 5[ppm]
X_points          = 65536
X_prescans        = 0
X_resolution      = 0.11455547[Hz]
X_sweep           = 7.50750751[kHz]
Clipped           = FALSE
Mod_return        = 1
Scans             = 8
Total_scans       = 8

X_90_width        = 10.5[us]
X_acq_time        = 0.7293952[s]
X_angle           = 45[deg]
X_pulse           = 9.25[us]
Initial_wait      = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 23
Relaxation_delay  = 14[s]
Temp_get          = 26.3[dC]
Unblank_time      = 2[us]
```


88



JEOL

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Filename          = H-T-ethyl-ketone-7.jd
Author            = delta
Experiment        = single_pulse.exp
Sample_id         = S#673304
Solvent           = CHLOROFORM-D
Creation_time     = 14-OCT-2008 02:15:40
Revision_time     =  3-NOV-2008 23:09:15
Current_time      =  3-NOV-2008 23:09:32

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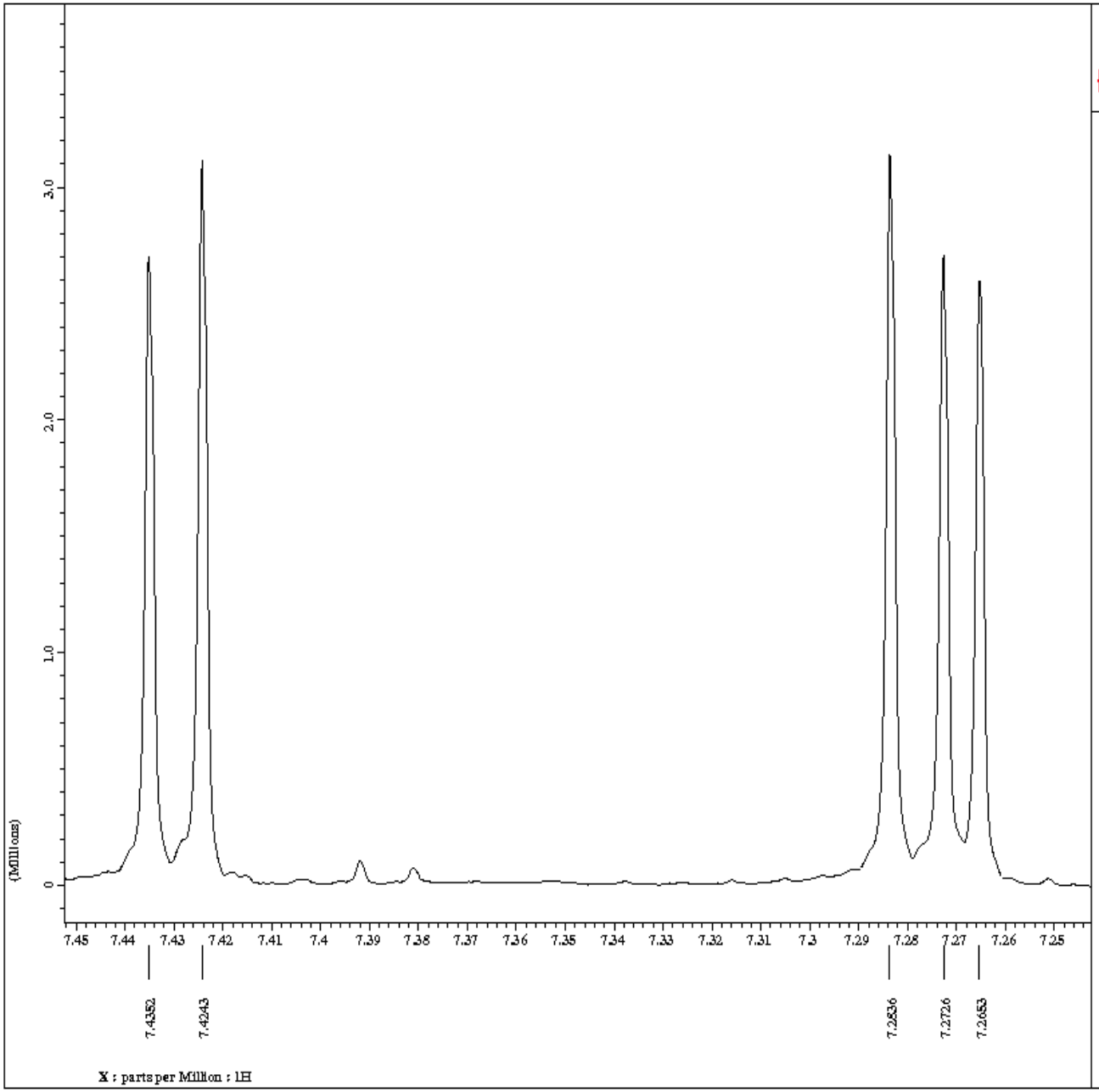
Data_format       = 1D COMPLEX
Dim_size          = 65536
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 0.7293952[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 5[ppm]
X_points          = 65536
X_prescans        = 0
X_resolution      = 0.11455547[Hz]
X_sweep           = 7.50750751[kHz]
Clipped           = FALSE
Mod_return        = 1
Scans             = 8
Total_scans       = 8

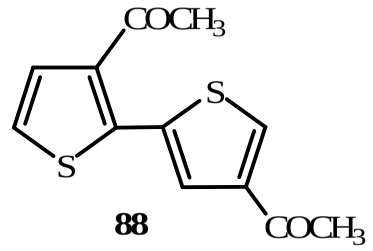
X_90_width        = 18.5[us]
X_acq_time        = 0.7293952[s]
X_angle           = 45[deg]
X_pulse           = 9.25[us]
Initial_wait      = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 20
Relaxation_delay  = 14[s]
Temp_get          = 26.6[dC]
Unblank_time      = 2[us]
```


88

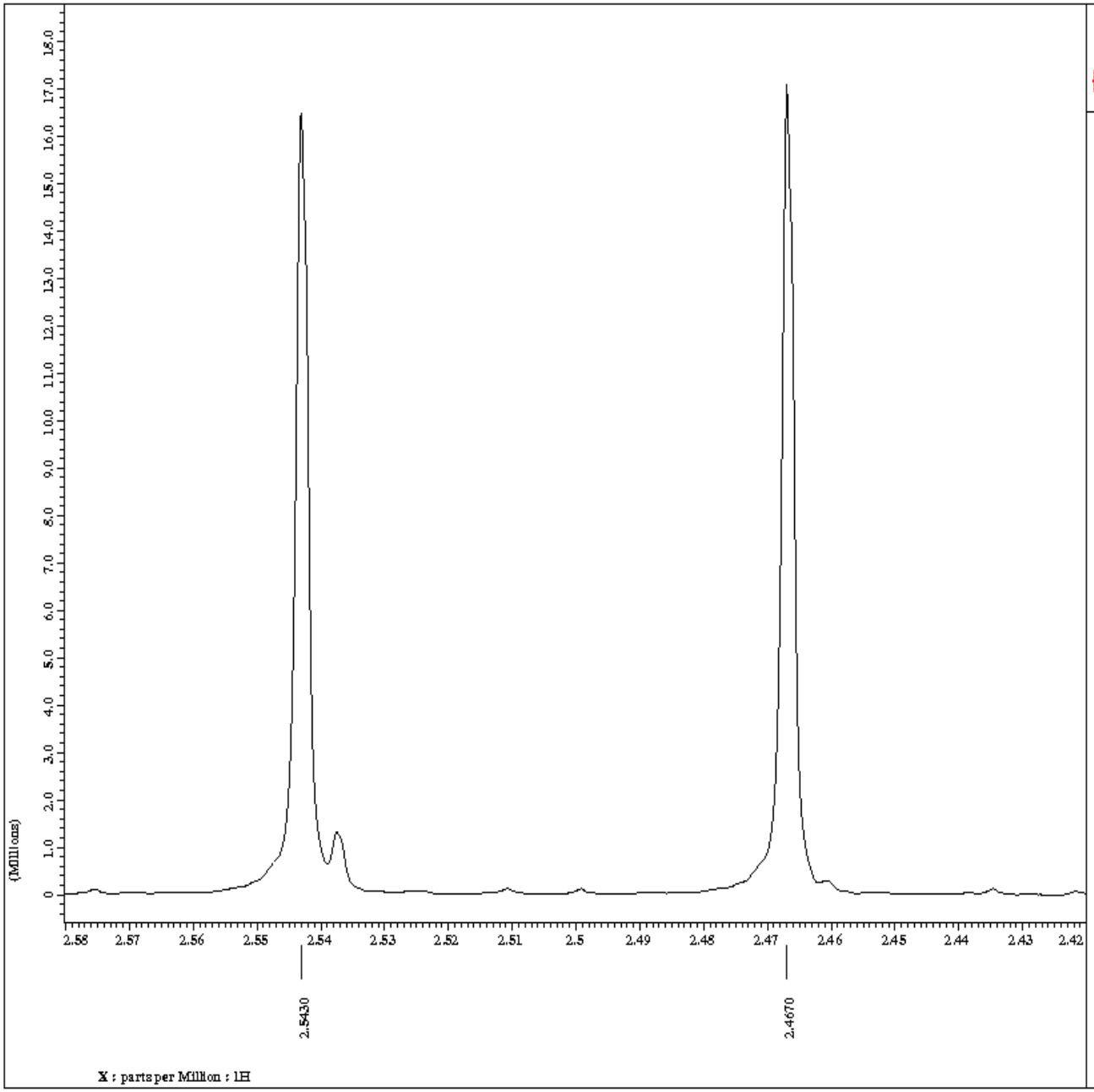


JEOL

Filename	= H-T-ethyl-ketone-7.jd
Author	= delta
Experiment	= single_pulse.exp
Sample_id	= S#673304
Solvent	= CHLOROFORM-D
Creation_time	= 14-OCT-2008 02:15:40
Revision_time	= 3-NOV-2008 23:09:55
Current_time	= 3-NOV-2008 23:10:09
Comment	= Single Pulse Experime
Data_format	= 1D COMPLEX
Dim_size	= 65536
Dim_title	= 1H
Dim_units	= [ppm]
Dimensions	= X
Site	= Eclipse+ 500
Spectrometer	= DELTA_NMR
Field_strength	= 11.7473579[T] (500[MH
X_acq_duration	= 0.7293952[s]
X_domain	= 1H
X_freq	= 500.15991521[MHz]
X_offset	= 5[ppm]
X_points	= 65536
X_prescans	= 0
X_resolution	= 0.1145554?[Hz]
X_sweep	= 7.50750751[kHz]
Clipped	= FALSE
Mod_return	= 1
Scans	= 8
Total_scans	= 8
X_90_width	= 10.5[us]
X_acq_time	= 0.7293952[s]
X_angle	= 45[deg]
X_pulse	= 9.25[us]
Initial_wait	= 1[s]
Phase_preset	= 3[us]
Recvr_gain	= 20
Relaxation_delay	= 14[s]
Temp_get	= 26.6[dC]
Unblank_time	= 2[us]

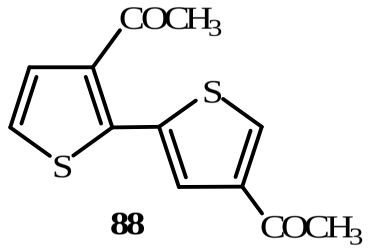


88

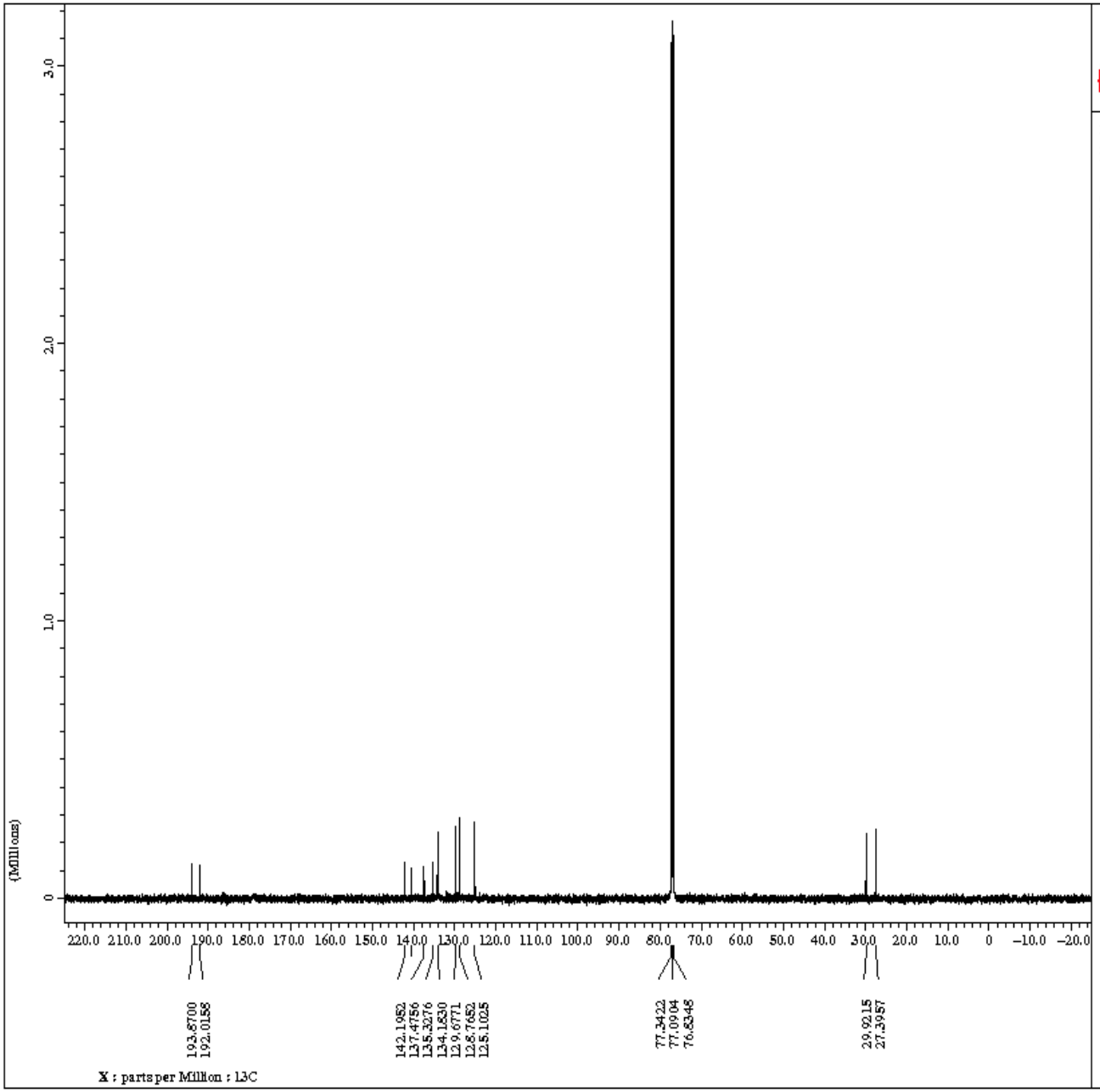


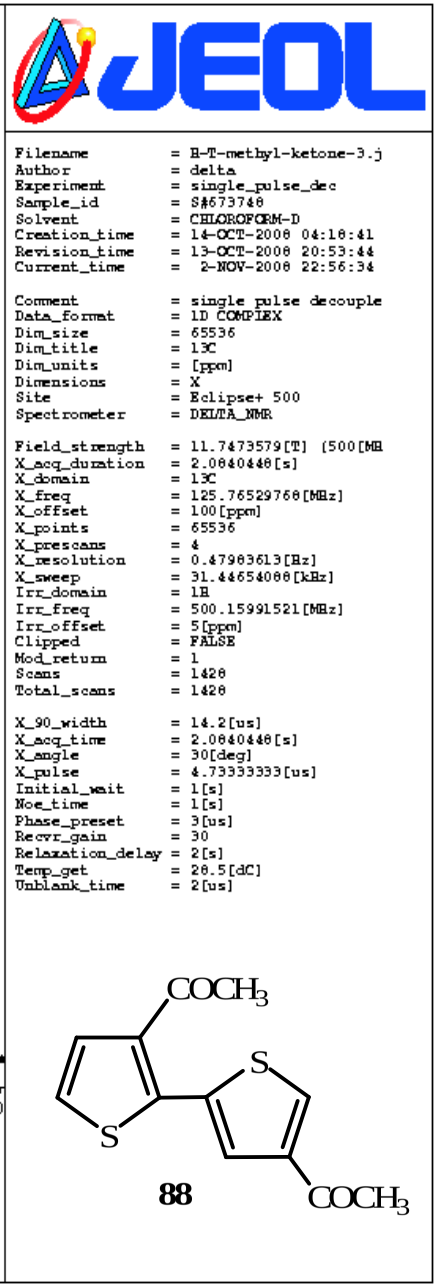
JEOL

Filename	= H-T-ethyl-ketone-7.jd
Author	= delta
Experiment	= single_pulse.exp
Sample_id	= S#673304
Solvent	= CHLOROFORM-D
Creation_time	= 14-OCT-2008 02:15:40
Revision_time	= 3-NOV-2008 23:10:36
Current_time	= 3-NOV-2008 23:10:52
Comment	= Single Pulse Experime
Data_format	= 1D COMPLEX
Dim_size	= 65536
Dim_title	= 1H
Dim_units	= [ppm]
Dimensions	= X
Site	= Eclipse+ 500
Spectrometer	= DELTA_NMR
Field_strength	= 11.7473579[T] (500[MH
X_acq_duration	= 0.7293952[s]
X_domain	= 1H
X_freq	= 500.15991521[MHz]
X_offset	= 5[ppm]
X_points	= 65536
X_prescans	= 0
X_resolution	= 0.11455547[Hz]
X_sweep	= 7.50750751[kHz]
Clipped	= FALSE
Mod_return	= 1
Scans	= 8
Total_scans	= 8
X_90_width	= 10.5[us]
X_acq_time	= 0.7293952[s]
X_angle	= 45[deg]
X_pulse	= 9.25[us]
Initial_wait	= 1[s]
Phase_preset	= 3[us]
Recvr_gain	= 20
Relaxation_delay	= 14[s]
Temp_get	= 26.6[dC]
Unblank_time	= 2[us]



88


(Millions)
3.0
2.0
1.0
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 −10.0 −20.0
193.8700
192.0158
142.1982
137.4756
135.3276
134.1830
129.6771
126.7682
125.1025
77.3422
77.0904
76.8348
29.9215
27.3957
X : parts per Million : 13C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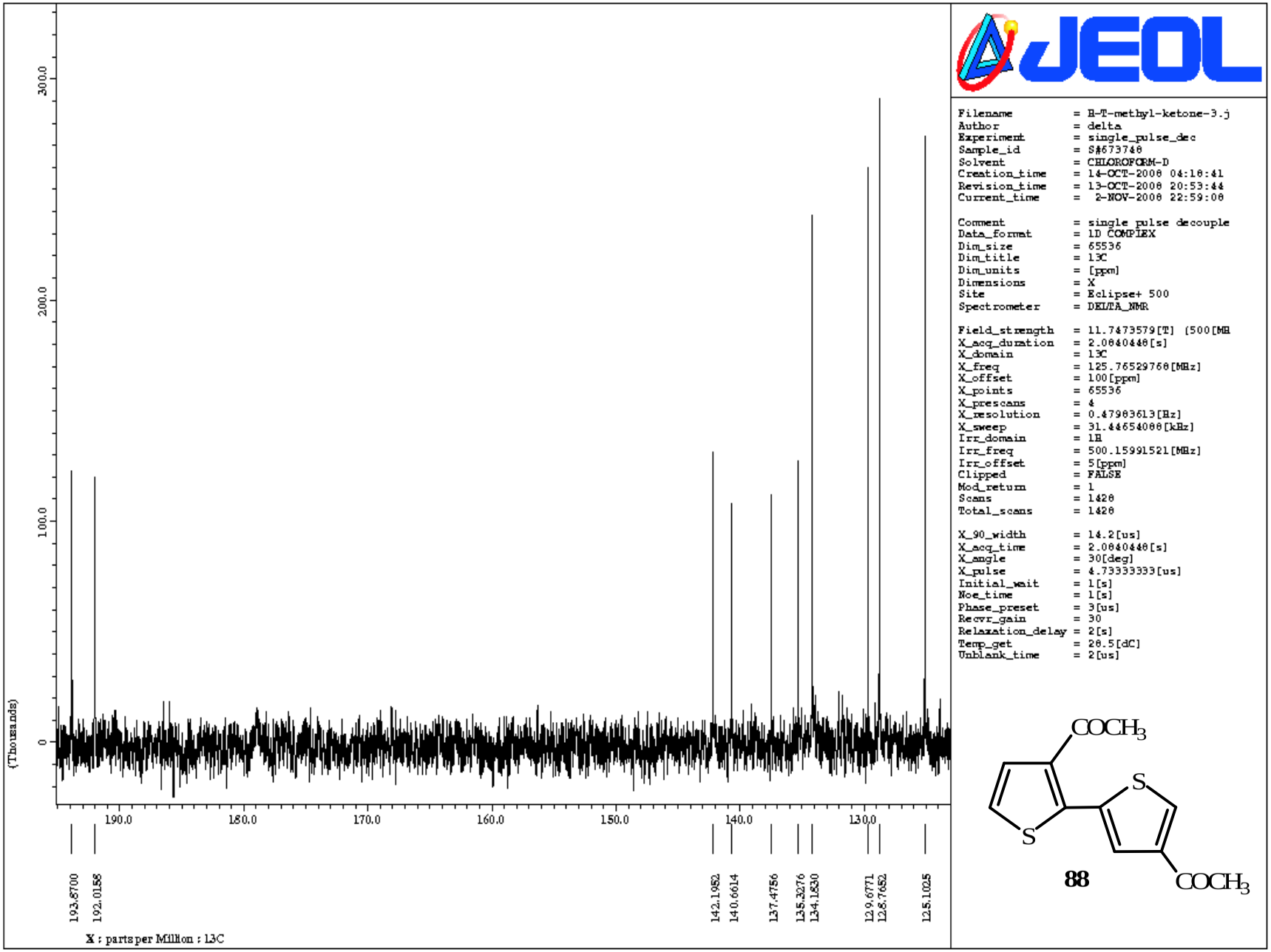
Author = delta
Experiment = single_pulse_dec
Sample_id = S#673740
Solvent = CHLOROFORM-D
Creation_time = 14-OCT-2008 04:18:41
Revision_time = 13-OCT-2008 20:53:44
Current_time = 2-NOV-2008 22:56:34
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 65536
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.0840448[s]
X_domain = 13C
X_freq = 125.76529768[MHz]
X_offset = 100[ppm]
X_points = 65536
X_prescans = 4
X_resolution = 0.47983613[Hz]
X_sweep = 31.44654088[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 1428
Total_scans = 1428
X_90_width = 14.2[us]
X_acq_time = 2.0840448[s]
X_angle = 30[deg]
X_pulse = 4.73333333[us]
Initial_wait = 1[s]
Noe_time = 1[s]
Phase_preset = 3[us]
Recvr_gain = 30
Relaxation_delay = 2[s]
Temp_get = 28.5[dC]
Unblank_time = 2[us]
COCH3
S
S
COCH3
88


300.0
200.0
100.0
0
(Thousands)
190.0
180.0
170.0
160.0
150.0
140.0
130.0
193.8700
192.0158
142.1952
140.6614
137.4756
135.3276
134.1830
129.6771
128.7652
125.1025
X : parts per Million : 13C
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Filename = H-T-methyl-ketone-3.j
Author = delta
Experiment = single_pulse_dec
Sample_id = S#673748
Solvent = CHLOROFORM-D
Creation_time = 14-OCT-2008 04:18:41
Revision_time = 13-OCT-2008 20:53:44
Current_time = 2-NOV-2008 22:59:08
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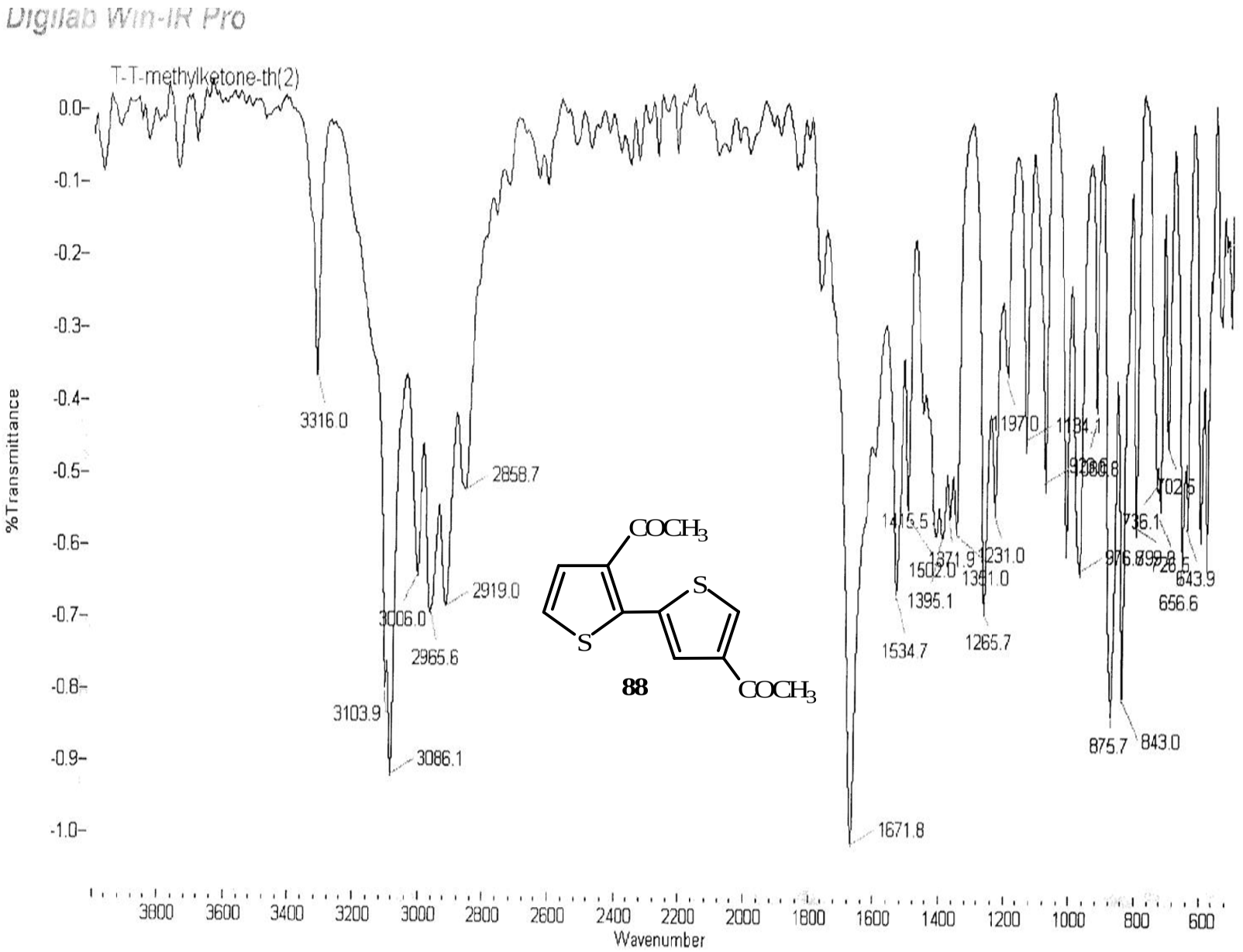
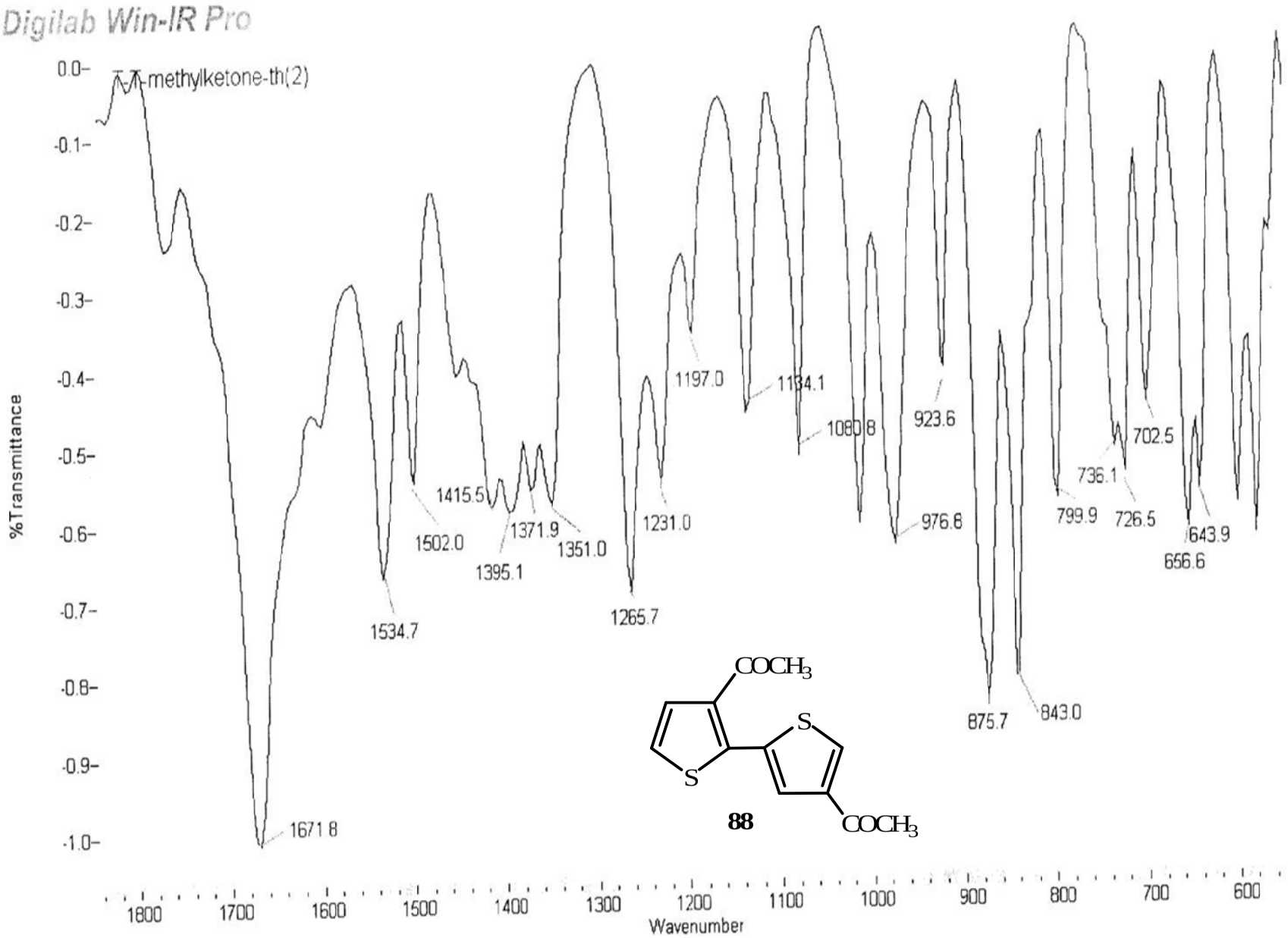
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.0840448[s]
X_domain = 13C
X_freq = 125.76529768[MHz]
X_offset = 100[ppm]
X_points = 65536
X_prescans = 4
X_resolution = 0.47983613[Hz]
X_sweep = 31.44654088[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 1420
Total_scans = 1420
X_90_width = 14.2[us]
X_acq_time = 2.0840448[s]
X_angle = 30[deg]
X_pulse = 4.73333333[us]
Initial_wait = 1[s]
Noe_time = 1[s]
Phase_preset = 3[us]
Recvr_gain = 30
Relaxation_delay = 2[s]
Temp_get = 28.5[dC]
Unblank_time = 2[us]
COCH3
S
S
COCH3
88

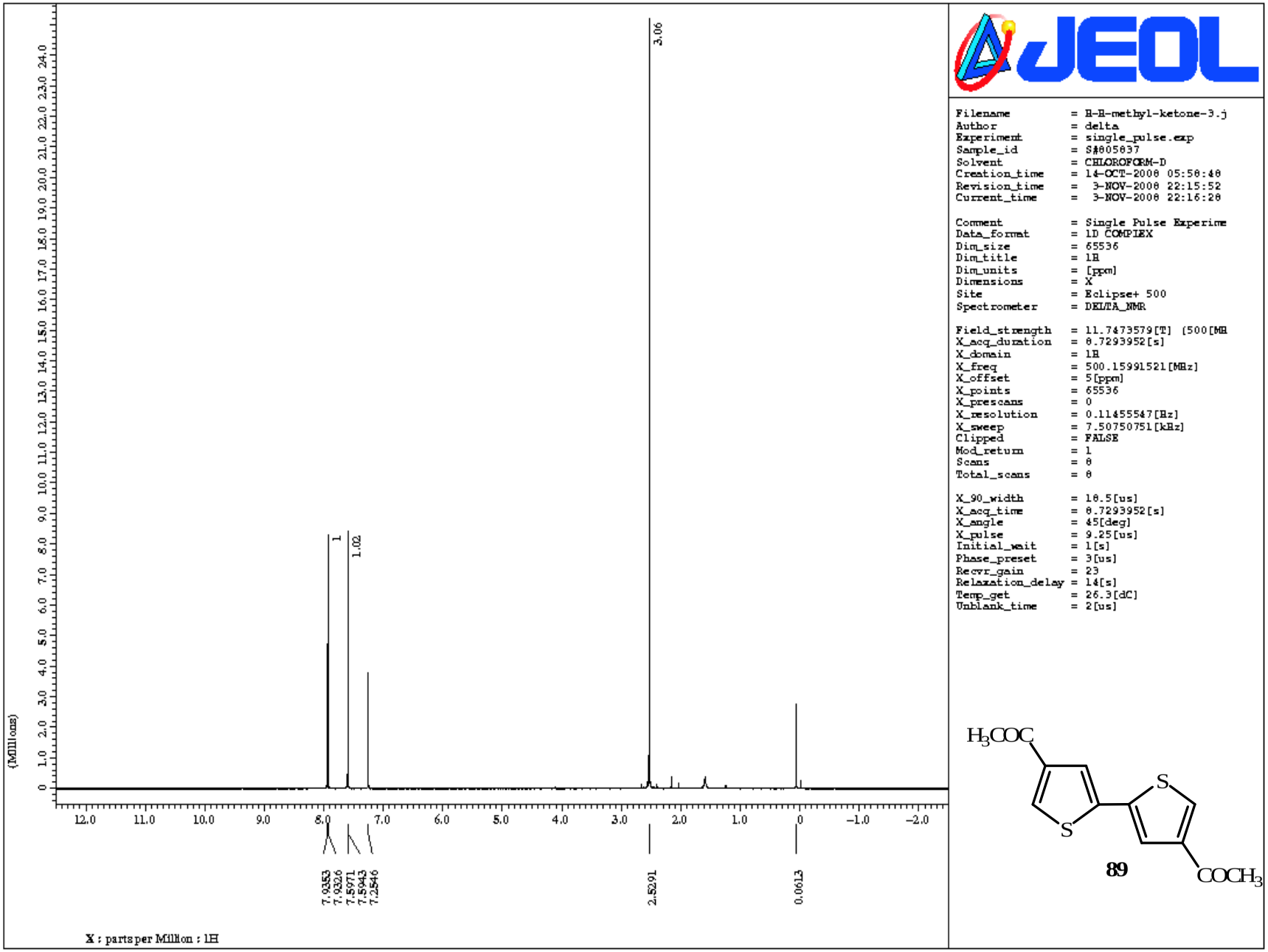

Digilab Win-IR Pro
T-T-methylketone-th(2)
%Transmittance
Wavenumber
3316.0
2858.7
2919.0
3006.0
2965.6
3103.9
3086.1
1671.8
1534.7
1502.0
1415.5
1395.1
1371.9
1361.0
1265.7
1231.0
1197.0
1134.1
875.7
843.0
736.1
656.6
643.9
COCH3
S
S
COCH3
88


Digilab Win-IR Pro
T-T-methylketone-th(2)
%Transmittance
0.0
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
-0.7
-0.8
-0.9
-1.0
1671.8
1534.7
1502.0
1415.5
1395.1
1371.9
1351.0
1265.7
1231.0
1197.0
1134.1
1080.8
976.8
923.6
875.7
843.0
799.9
736.1
726.5
702.5
656.6
643.9
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
Wavenumber
COCH3
S
S
COCH3

88

APPENDIX 12

^{1}H, ^{13}C NMR and IR spectra of 4,4'-diethanoyl -2,2'-bithiophene (**89**)


(Millions)
3.06
1
1.02
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
7.9353
7.9326
7.5971
7.5943
7.2546
2.5291
0.0613
X : parts per Million : 1H
JEOL
Filename = H-H-methyl-ketone-3.j
Author = delta
Experiment = single_pulse.exp
Sample_id = S#805037
Solvent = CHLOROFORM-D
Creation_time = 14-OCT-2008 05:58:48
Revision_time = 3-NOV-2008 22:15:52
Current_time = 3-NOV-2008 22:16:28
Comment = Single Pulse Experime
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Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
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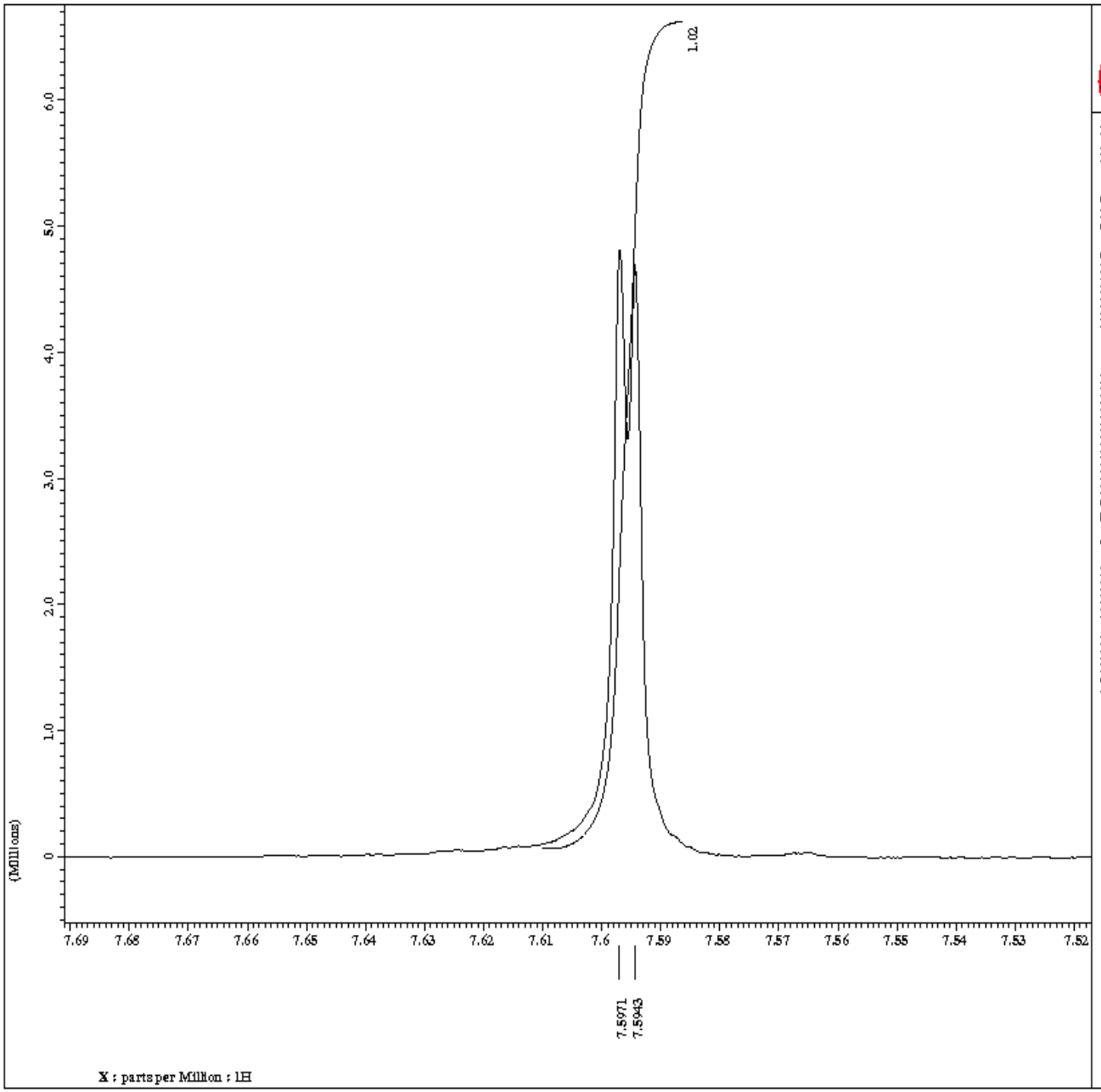
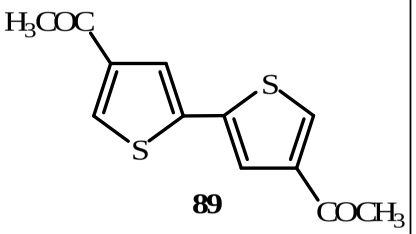
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 0.7293952[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 65536
X_prescans = 0
X_resolution = 0.11455547[Hz]
X_sweep = 7.50750751[kHz]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 10.5[us]
X_acq_time = 0.7293952[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 23
Relaxation_delay = 14[s]
Temp_get = 26.3[dC]
Unblank_time = 2[us]
H3COC
S
S
COCH3
89

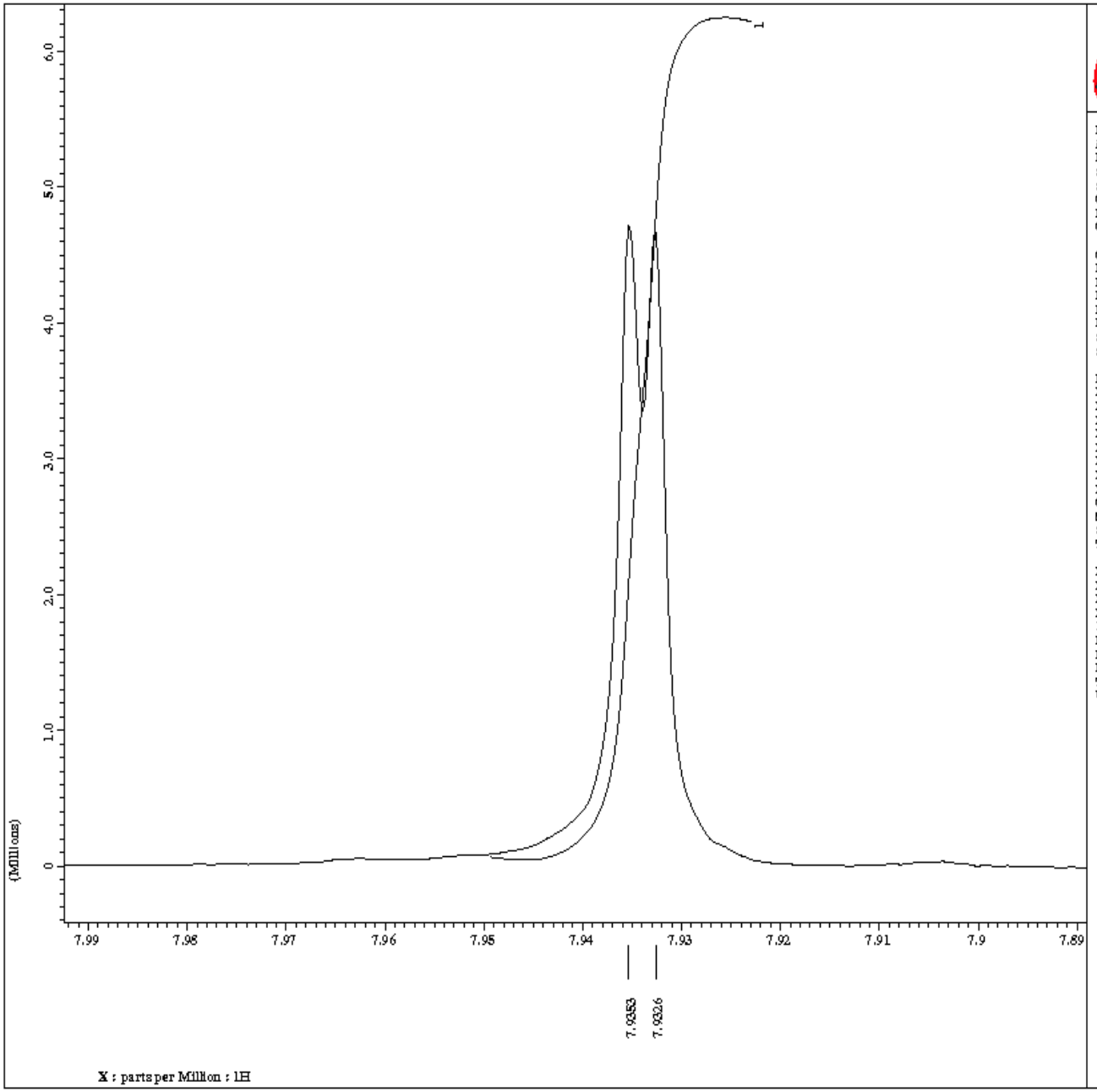


JEOL

Filename	= H-H-methyl-ketone-3.j
Author	= delta
Experiment	= single_pulse.exp
Sample_id	= S#005037
Solvent	= CHLOROFORM-D
Creation_time	= 14-OCT-2008 05:58:48
Revision_time	= 3-NOV-2008 22:15:52
Current_time	= 3-NOV-2008 22:22:42
Comment	= Single Pulse Experime
Data_format	= 1D COMPLEX
Dim_size	= 65536
Dim_title	= 1H
Dim_units	= [ppm]
Dimensions	= X
Site	= Eclipse+ 500
Spectrometer	= DELTA_NMR
Field_strength	= 11.7473579[T] (500[MH
X_acq_duration	= 0.7293952[s]
X_domain	= 1H
X_freq	= 500.15991521[MHz]
X_offset	= 5[ppm]
X_points	= 65536
X_prescans	= 0
X_resolution	= 0.11455547[Hz]
X_sweep	= 7.50750751[kHz]
Clipped	= FALSE
Mod_return	= 1
Scans	= 8
Total_scans	= 8
X_90_width	= 10.5[us]
X_acq_time	= 0.7293952[s]
X_angle	= 45[deg]
X_pulse	= 9.25[us]
Initial_wait	= 1[s]
Phase_preset	= 3[us]
Recvr_gain	= 23
Relaxation_delay	= 14[s]
Temp_get	= 26.3[dC]
Unblank_time	= 2[us]



89



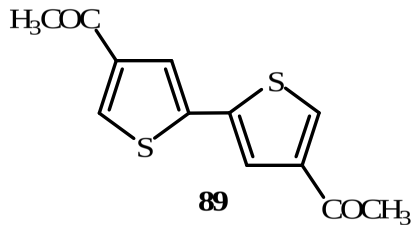
JEOL

```
Filename          = H-H-methyl-ketone-3.j
Author            = delta
Experiment        = single_pulse.exp
Sample_id         = S#805037
Solvent           = CHLOROFORM-D
Creation_time     = 14-OCT-2008 05:58:48
Revision_time     =  3-NOV-2008 22:15:52
Current_time      =  3-NOV-2008 22:20:11

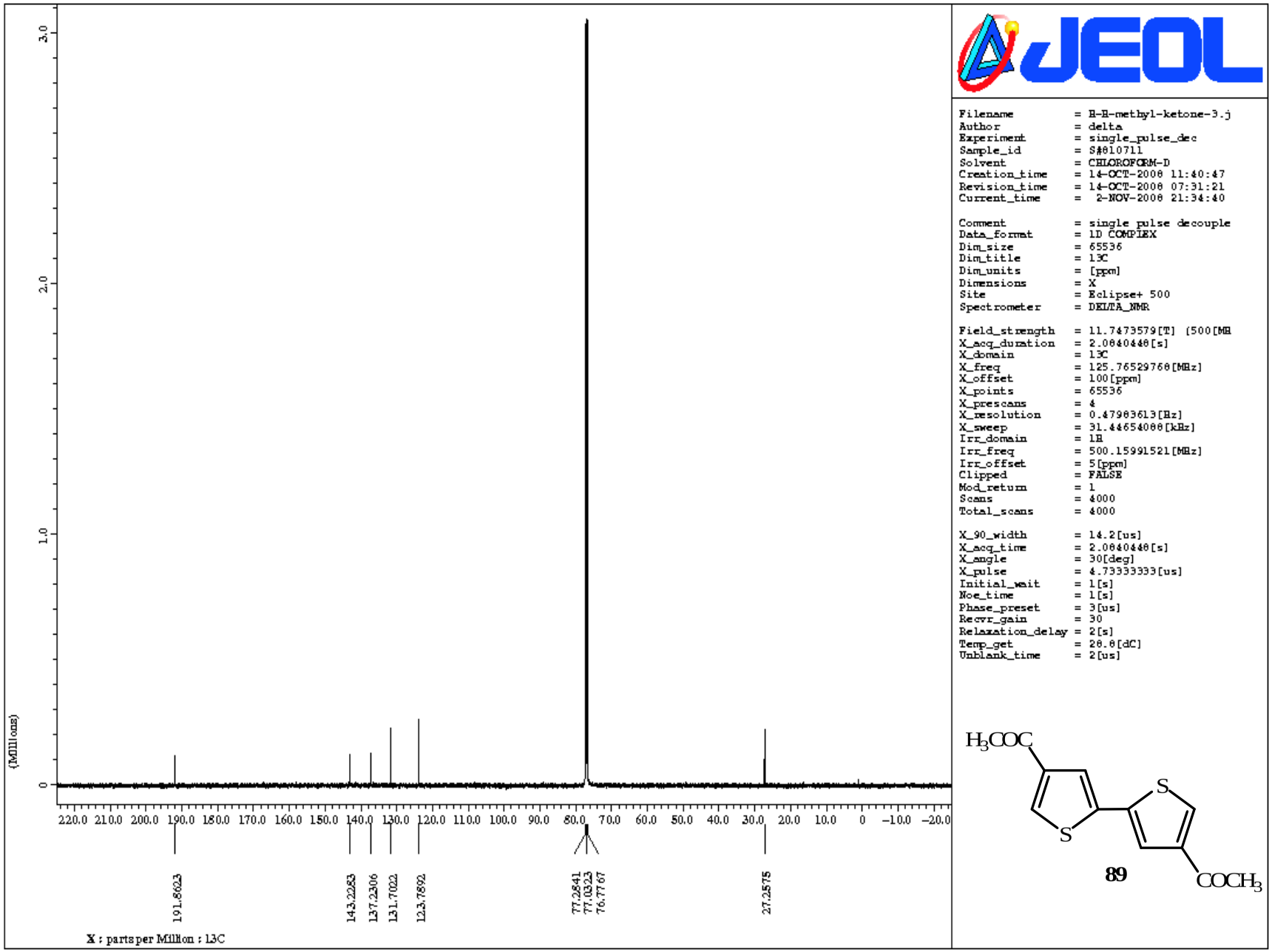
Comment           = Single Pulse Experime
Data_format       = 1D COMPLEX
Dim_size          = 65536
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

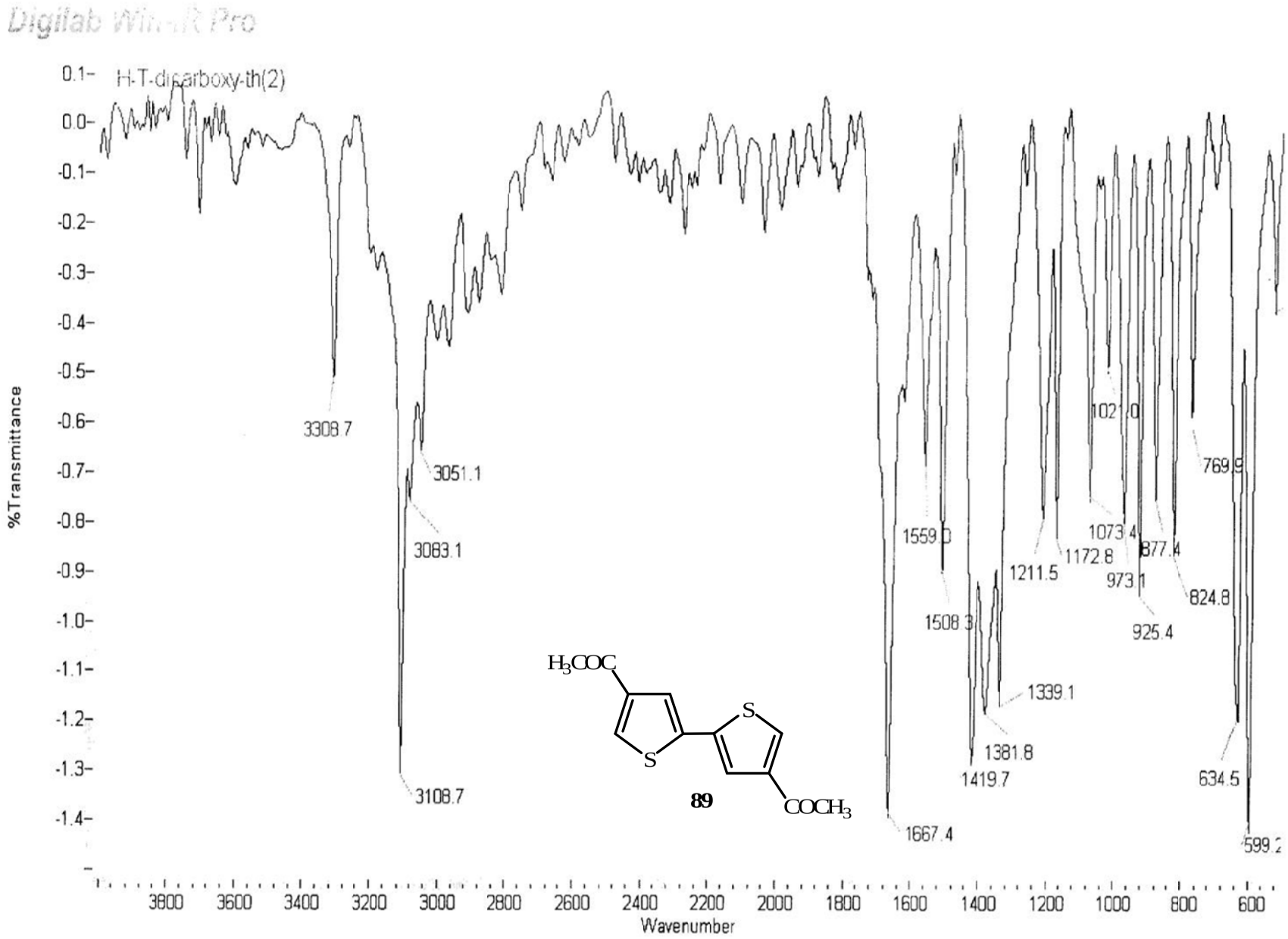
Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 0.7293952[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 5[ppm]
X_points          = 65536
X_prescans        = 0
X_resolution      = 0.11455547[Hz]
X_sweep           = 7.50750751[kHz]
Clipped           = FALSE
Mod_return        = 1
Scans             = 8
Total_scans       = 8

X_90_width        = 10.5[us]
X_acq_time        = 0.7293952[s]
X_angle           = 45[deg]
X_pulse           = 9.25[us]
Initial_wait      = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 23
Relaxation_delay  = 14[s]
Temp_get          = 26.3[dC]
Unblank_time      = 2[us]
```



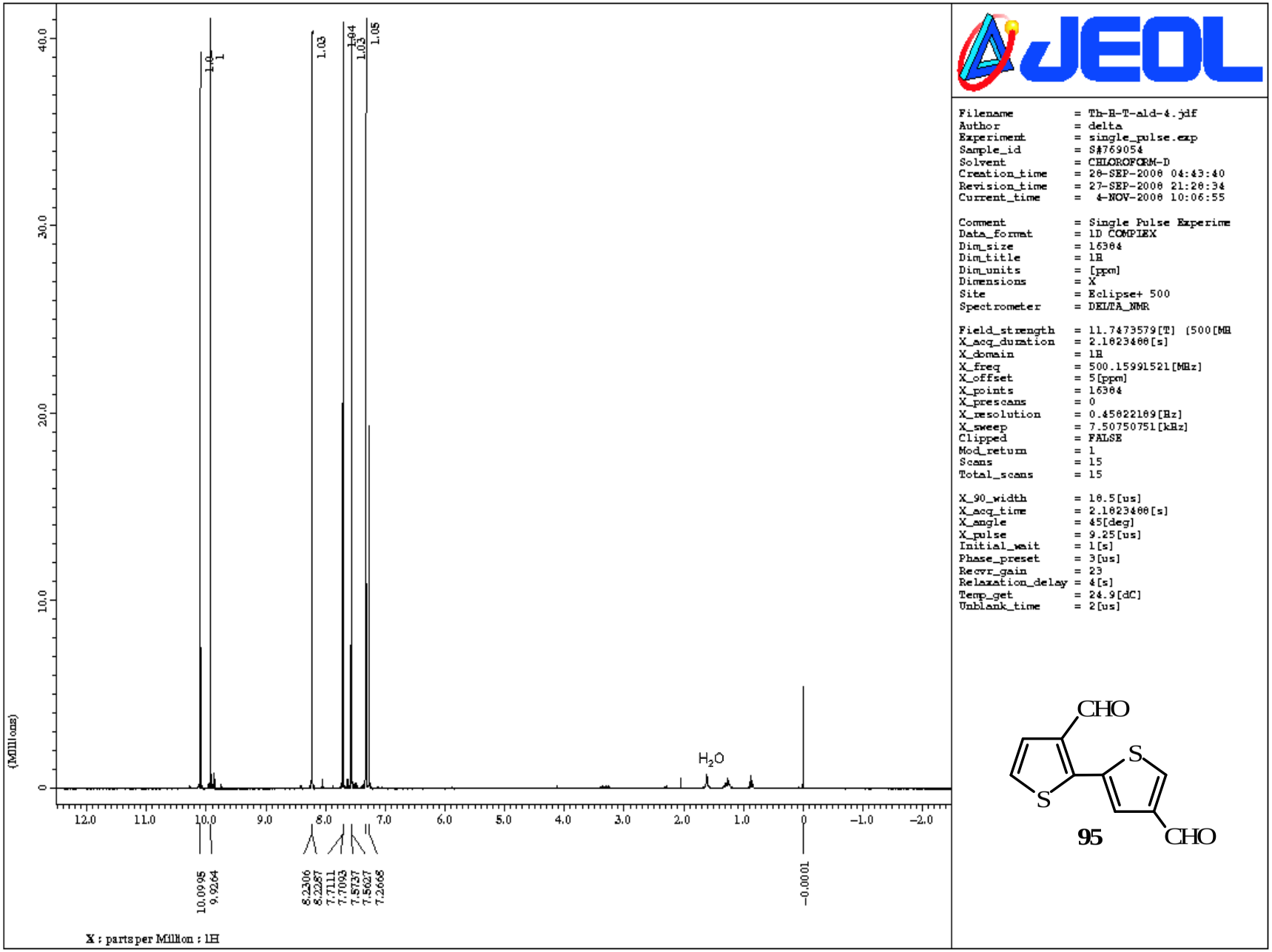
89

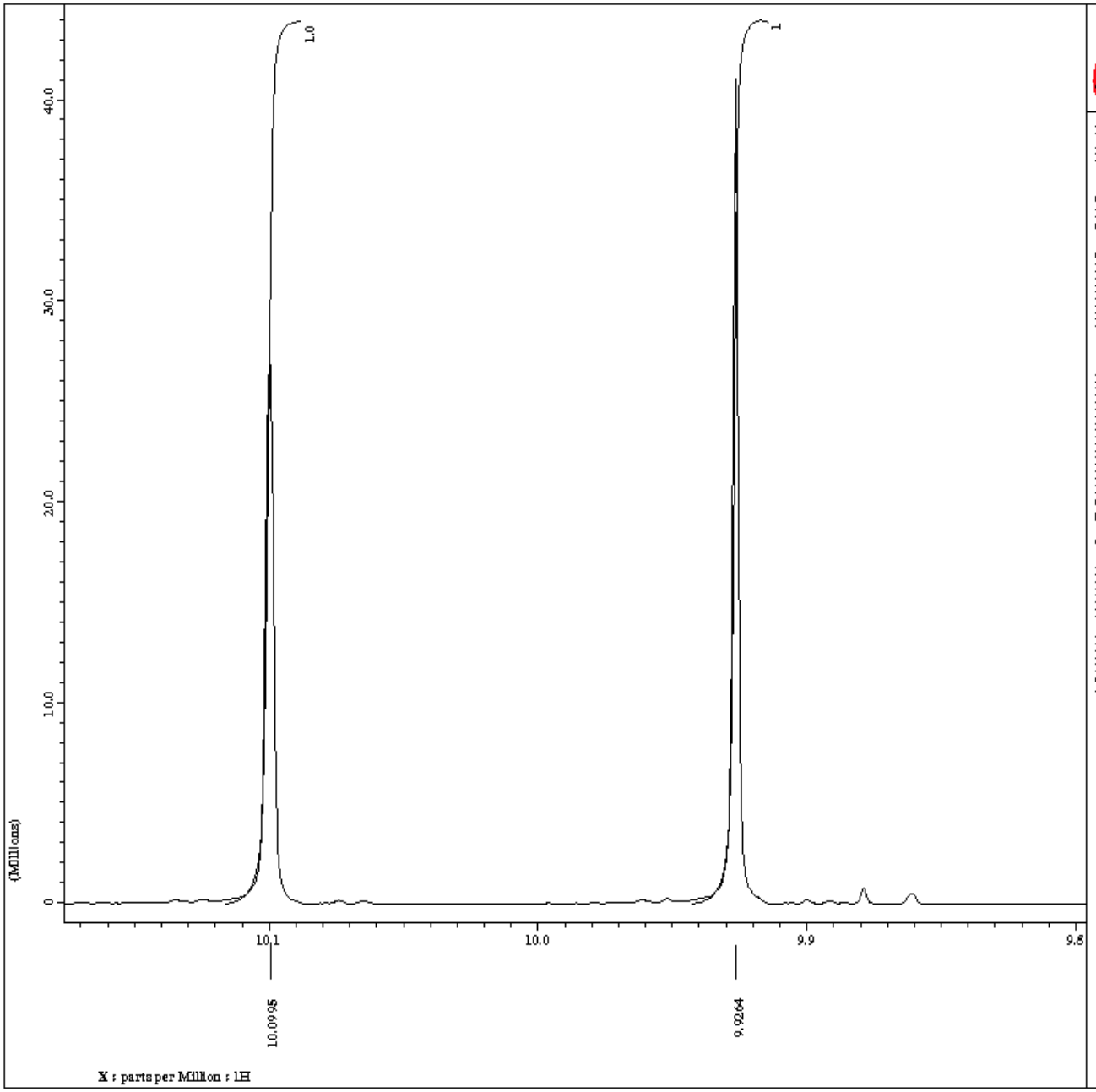

3.0
2.0
1.0
0
(Millions)
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 −10.0 −20.0
191.8623
143.2283
137.2306
131.7022
128.7892
77.2841
77.0323
76.7767
27.2575
X : parts per Million : 13C
JEOL
Filename = H-H-methyl-ketone-3.j
Author = delta
Experiment = single_pulse_dec
Sample_id = S#010711
Solvent = CHLOROFORM-D
Creation_time = 14-OCT-2008 11:40:47
Revision_time = 14-OCT-2008 07:31:21
Current_time = 2-NOV-2008 21:34:40
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 65536
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.0840448[s]
X_domain = 13C
X_freq = 125.76529768[MHz]
X_offset = 100[ppm]
X_points = 65536
X_prescans = 4
X_resolution = 0.47983613[Hz]
X_sweep = 31.44654088[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 4000
Total_scans = 4000
X_90_width = 14.2[us]
X_acq_time = 2.0840448[s]
X_angle = 30[deg]
X_pulse = 4.73333333[us]
Initial_wait = 1[s]
Noe_time = 1[s]
Phase_preset = 3[us]
Recvr_gain = 30
Relaxation_delay = 2[s]
Temp_get = 28.8[dC]
Unblank_time = 2[us]
H3COC
S
S
COCH3
89


Digilab Win-IR Pro
H-T-dicarboxy-th(2)
%Transmittance
Wavenumber
3308.7
3108.7
3083.1
3051.1
1667.4
1559.0
1508.3
1419.7
1381.8
1339.1
1211.5
1172.8
1073.4
1021.0
973.1
925.4
877.4
824.8
769.9
634.5
599.2
89

APPENDIX 13

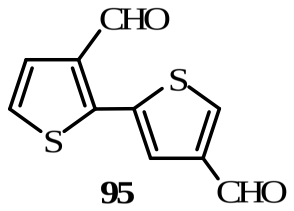
^{1}H, ^{13}C NMR and IR spectra of 2,2'-bithiophene-3,4'-dicarbaldehyde (**95**)


JEOL
Filename = Th-H-T-ald-4.jdf
Author = delta
Experiment = single_pulse.exp
Sample_id = S#769054
Solvent = CHLOROFORM-D
Creation_time = 26-SEP-2008 04:43:40
Revision_time = 27-SEP-2008 21:26:34
Current_time = 4-NOV-2008 10:06:55
Comment = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Clipped = FALSE
Mod_return = 1
Scans = 15
Total_scans = 15
X_90_width = 18.5[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 23
Relaxation_delay = 4[s]
Temp_get = 24.9[dC]
Unblank_time = 2[us]
(Millions)
40.0
30.0
20.0
10.0
0
1.00
1.03
1.04
1.03
1.05
H2O
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
10.0995
9.9264
8.2306
8.2287
7.7111
7.7093
7.5737
7.5627
7.2668
-0.0001
X : parts per Million : 1H
CHO
S
S
CHO
95

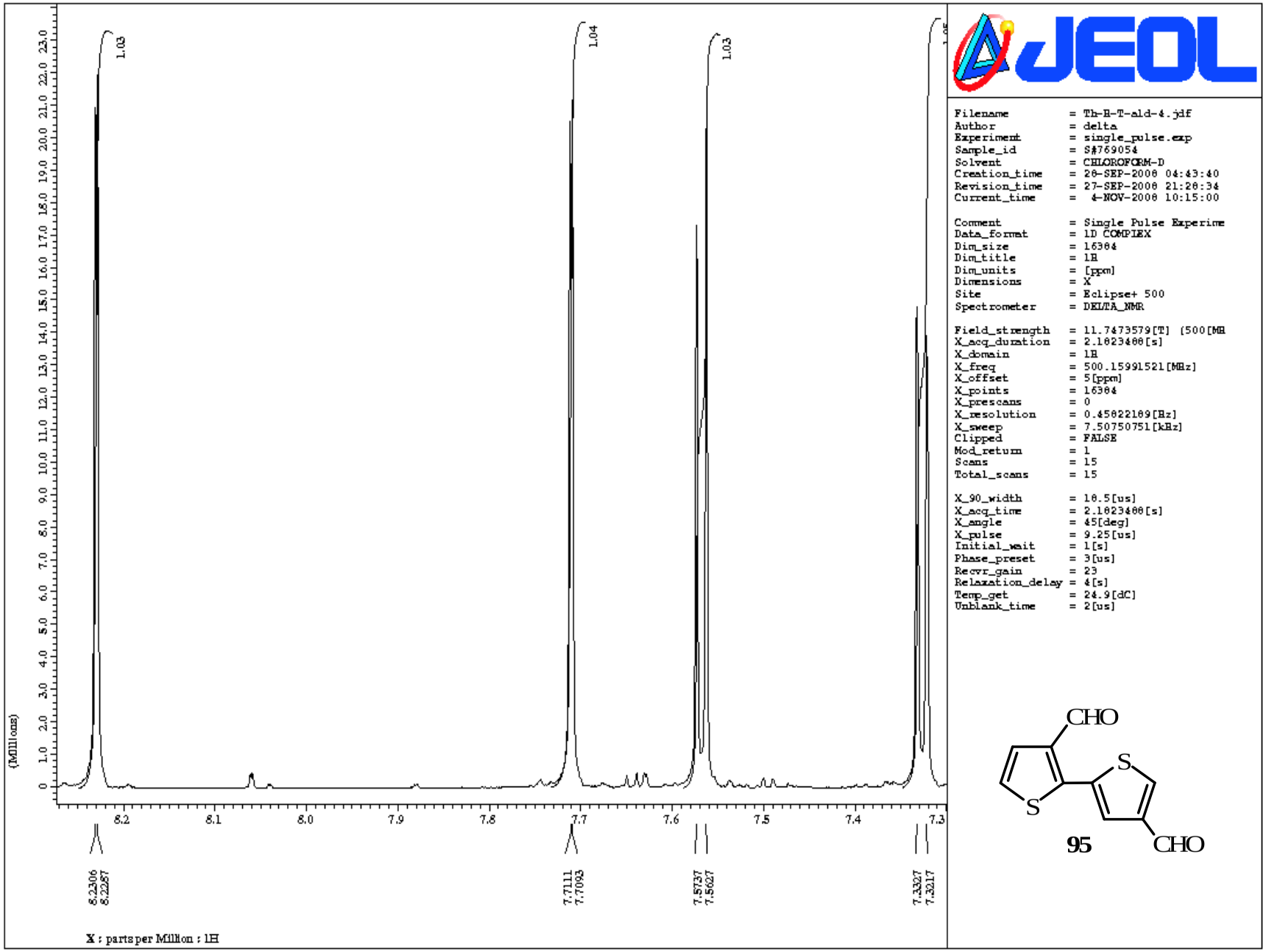


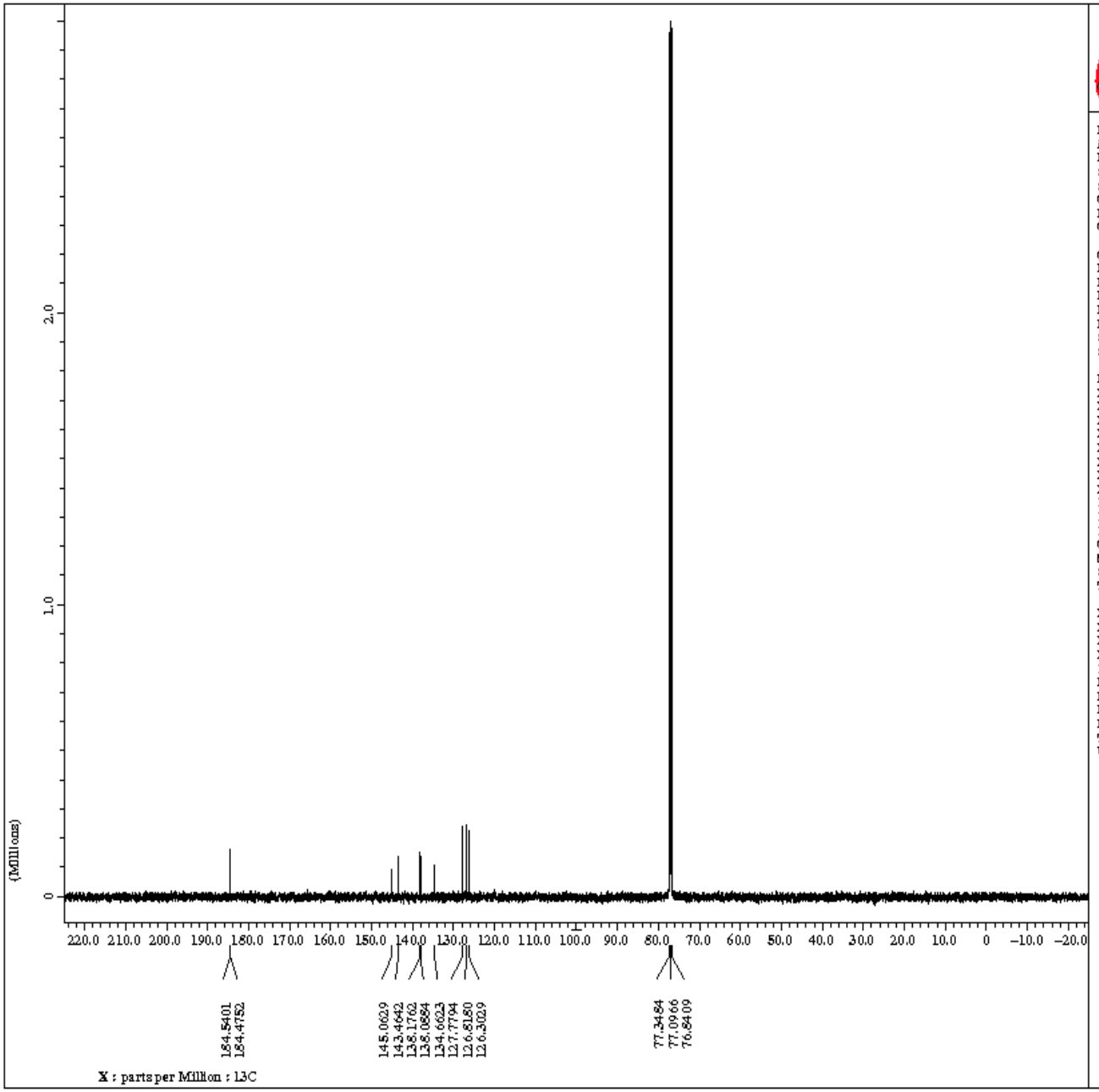
JEOL

Filename	= Th-H-T-ald-4.jdf
Author	= delta
Experiment	= single_pulse.exp
Sample_id	= S#769054
Solvent	= CHLOROFORM-D
Creation_time	= 26-SEP-2008 04:43:40
Revision_time	= 27-SEP-2008 21:26:34
Current_time	= 4-NOV-2008 10:11:01
Comment	= Single Pulse Experime
Data_format	= 1D COMPLEX
Dim_size	= 16384
Dim_title	= 1H
Dim_units	= [ppm]
Dimensions	= X
Site	= Eclipse+ 500
Spectrometer	= DELTA_NMR
Field_strength	= 11.7473579[T] (500[MH
X_acq_duration	= 2.1023488[s]
X_domain	= 1H
X_freq	= 500.15991521[MHz]
X_offset	= 5[ppm]
X_points	= 16384
X_prescans	= 0
X_resolution	= 0.45822189[Hz]
X_sweep	= 7.50750751[kHz]
Clipped	= FALSE
Mod_return	= 1
Scans	= 15
Total_scans	= 15
X_90_width	= 10.5[us]
X_acq_time	= 2.1023488[s]
X_angle	= 45[deg]
X_pulse	= 9.25[us]
Initial_wait	= 1[s]
Phase_preset	= 3[us]
Recvr_gain	= 23
Relaxation_delay	= 4[s]
Temp_get	= 24.9[dC]
Unblank_time	= 2[us]



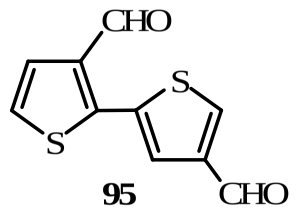
95


1.03
1.04
1.03
(Millions)
8.2306
8.2287
7.7111
7.7093
7.5737
7.5627
7.3327
7.3217
X : parts per Million : 1H
Filename = Th-H-T-ald-4.jdf
Author = delta
Experiment = single_pulse.exp
Sample_id = S#769054
Solvent = CHLOROFORM-D
Creation_time = 26-SEP-2008 04:43:40
Revision_time = 27-SEP-2008 21:28:34
Current_time = 4-NOV-2008 10:15:00
Comment = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822169[Hz]
X_sweep = 7.50750751[kHz]
Clipped = FALSE
Mod_return = 1
Scans = 15
Total_scans = 15
X_90_width = 10.5[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 23
Relaxation_delay = 4[s]
Temp_get = 24.9[dC]
Unblank_time = 2[us]
CHO
S
S
CHO
95

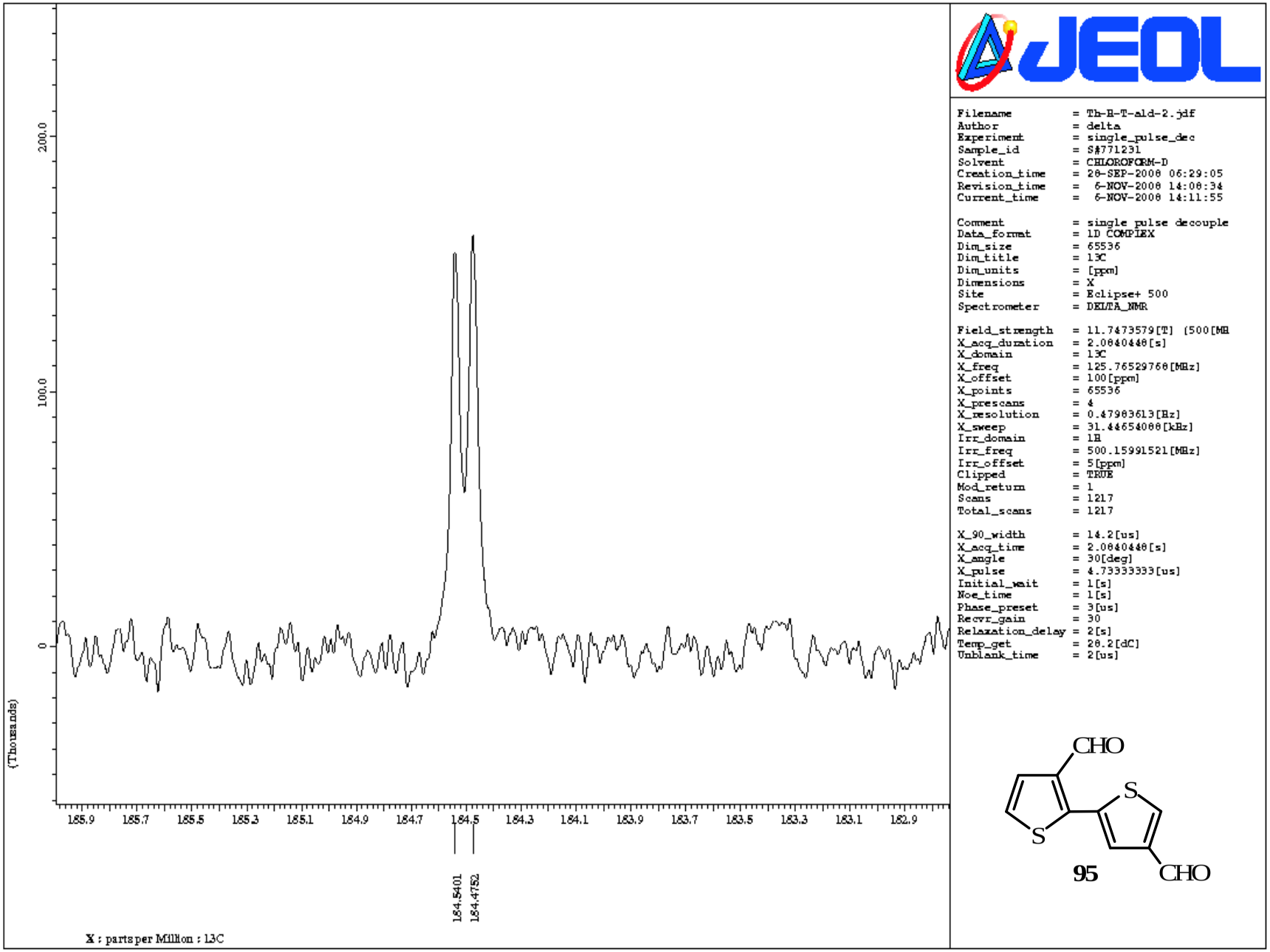


JEOL

Filename	= Th-B-T-ald-2.jdf
Author	= delta
Experiment	= single_pulse_dec
Sample_id	= S#771231
Solvent	= CHLOROFORM-D
Creation_time	= 28-SEP-2008 06:29:05
Revision_time	= 6-NOV-2008 14:08:34
Current_time	= 6-NOV-2008 14:09:05
Comment	= single pulse decouple
Data_format	= 1D COMPLEX
Dim_size	= 65536
Dim_title	= 13C
Dim_units	= [ppm]
Dimensions	= X
Site	= Eclipse+ 500
Spectrometer	= DELTA_NMR
Field_strength	= 11.7473579[T] (500[MH
X_acq_duration	= 2.0840448[s]
X_domain	= 13C
X_freq	= 125.76529768[MHz]
X_offset	= 100[ppm]
X_points	= 65536
X_prescans	= 4
X_resolution	= 0.47983613[Hz]
X_sweep	= 31.44654088[kHz]
Irr_domain	= 1H
Irr_freq	= 500.15991521[MHz]
Irr_offset	= 5[ppm]
Clipped	= TRUE
Mod_return	= 1
Scans	= 1217
Total_scans	= 1217
X_90_width	= 14.2[us]
X_acq_time	= 2.0840448[s]
X_angle	= 30[deg]
X_pulse	= 4.73333333[us]
Initial_wait	= 1[s]
Noe_time	= 1[s]
Phase_preset	= 3[us]
Recvr_gain	= 30
Relaxation_delay	= 2[s]
Temp_get	= 28.2[dC]
Unblank_time	= 2[us]



95



JEOL

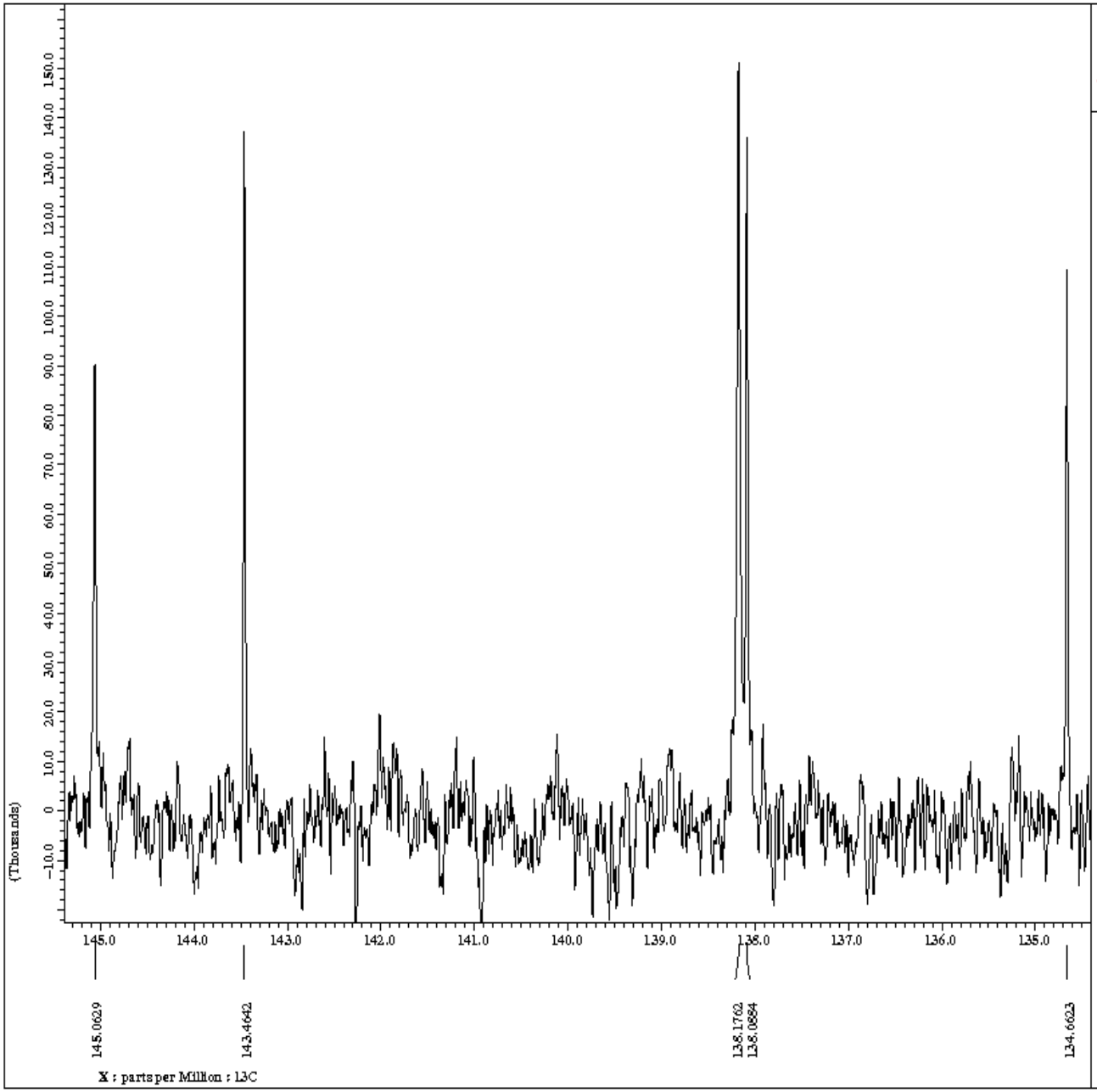
```
Filename          = Th-H-T-ald-2.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#771231
Solvent           = CHLOROFORM-D
Creation_time     = 28-SEP-2008 06:29:05
Revision_time     =  6-NOV-2008 14:08:34
Current_time      =  6-NOV-2008 14:11:55

Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 65536
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 2.0840448[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 65536
X_prescans        = 4
X_resolution      = 0.47983613[Hz]
X_sweep           = 31.44654088[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5[ppm]
Clipped           = TRUE
Mod_return        = 1
Scans             = 1217
Total_scans       = 1217

X_90_width        = 14.2[us]
X_acq_time        = 2.0840448[s]
X_angle           = 30[deg]
X_pulse           = 4.73333333[us]
Initial_wait      = 1[s]
Noe_time          = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 30
Relaxation_delay  = 2[s]
Temp_get          = 28.2[dC]
Unblank_time      = 2[us]
```


95



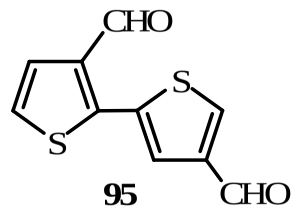
JEOL

```
Filename          = Th-B-T-ald-2.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#771231
Solvent           = CHLOROFORM-D
Creation_time     = 28-SEP-2008 06:29:05
Revision_time     =  6-NOV-2008 14:08:34
Current_time      =  6-NOV-2008 14:16:13

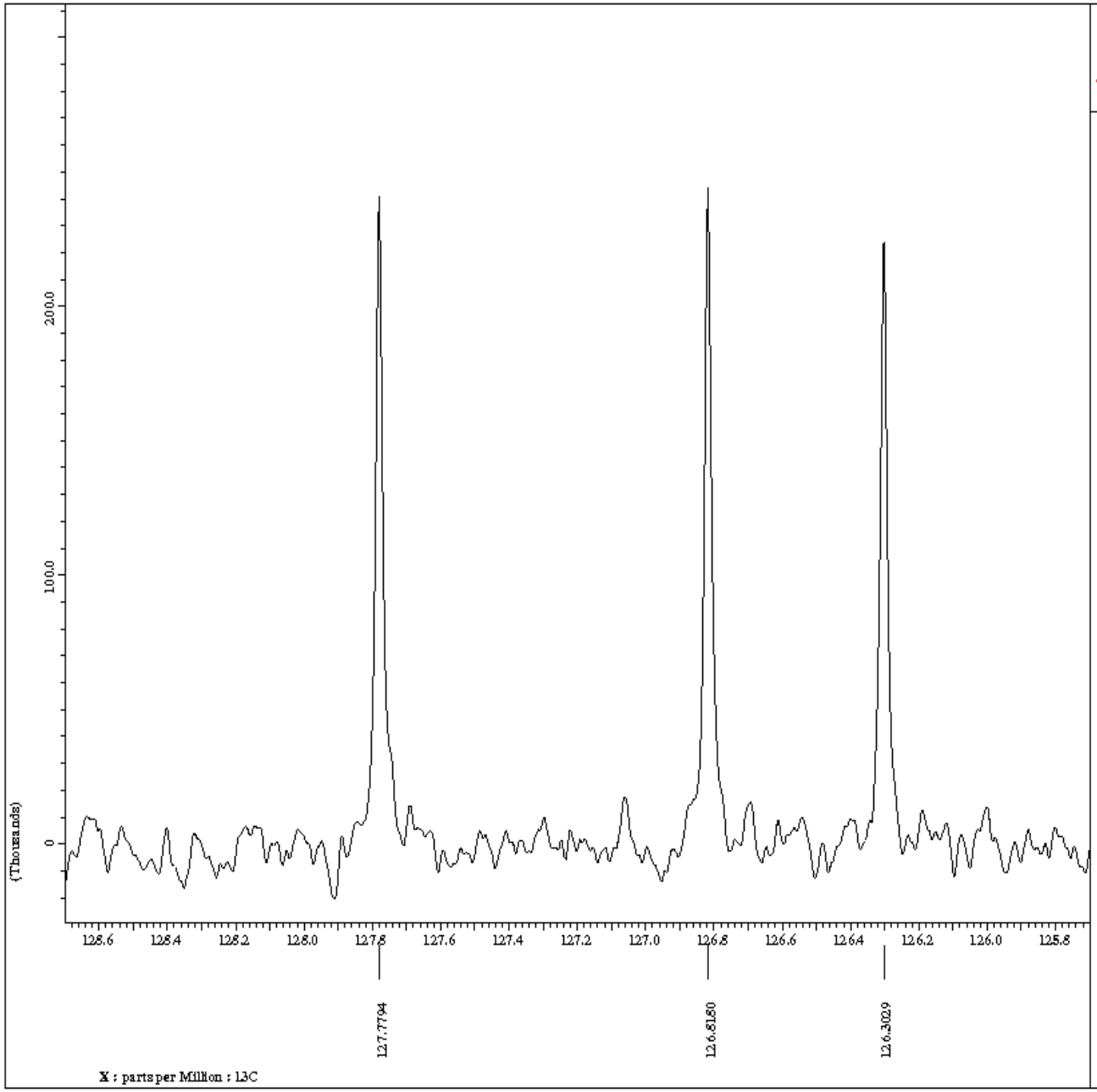
Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 65536
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 2.0840448[s]
X_domain          = 13C
X_freq            = 125.76529760[MHz]
X_offset          = 100[ppm]
X_points          = 65536
X_prescans        = 4
X_resolution      = 0.47983613[Hz]
X_sweep           = 31.44654088[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5[ppm]
Clipped           = TRUE
Mod_return        = 1
Scans             = 1217
Total_scans       = 1217

X_90_width        = 14.2[us]
X_acq_time        = 2.0840448[s]
X_angle           = 30[deg]
X_pulse           = 4.73333333[us]
Initial_wait      = 1[s]
Noe_time          = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 30
Relaxation_delay  = 2[s]
Temp_get          = 28.2[dC]
Unblank_time      = 2[us]
```



95



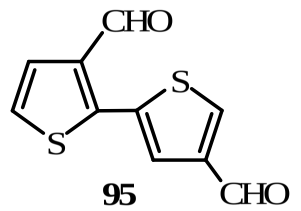
JEOL

```
Filename          = Th-H-T-ald-2.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#771231
Solvent           = CHLOROFORM-D
Creation_time     = 28-SEP-2008 06:29:05
Revision_time     =  6-NOV-2008 14:08:34
Current_time      =  6-NOV-2008 14:17:53

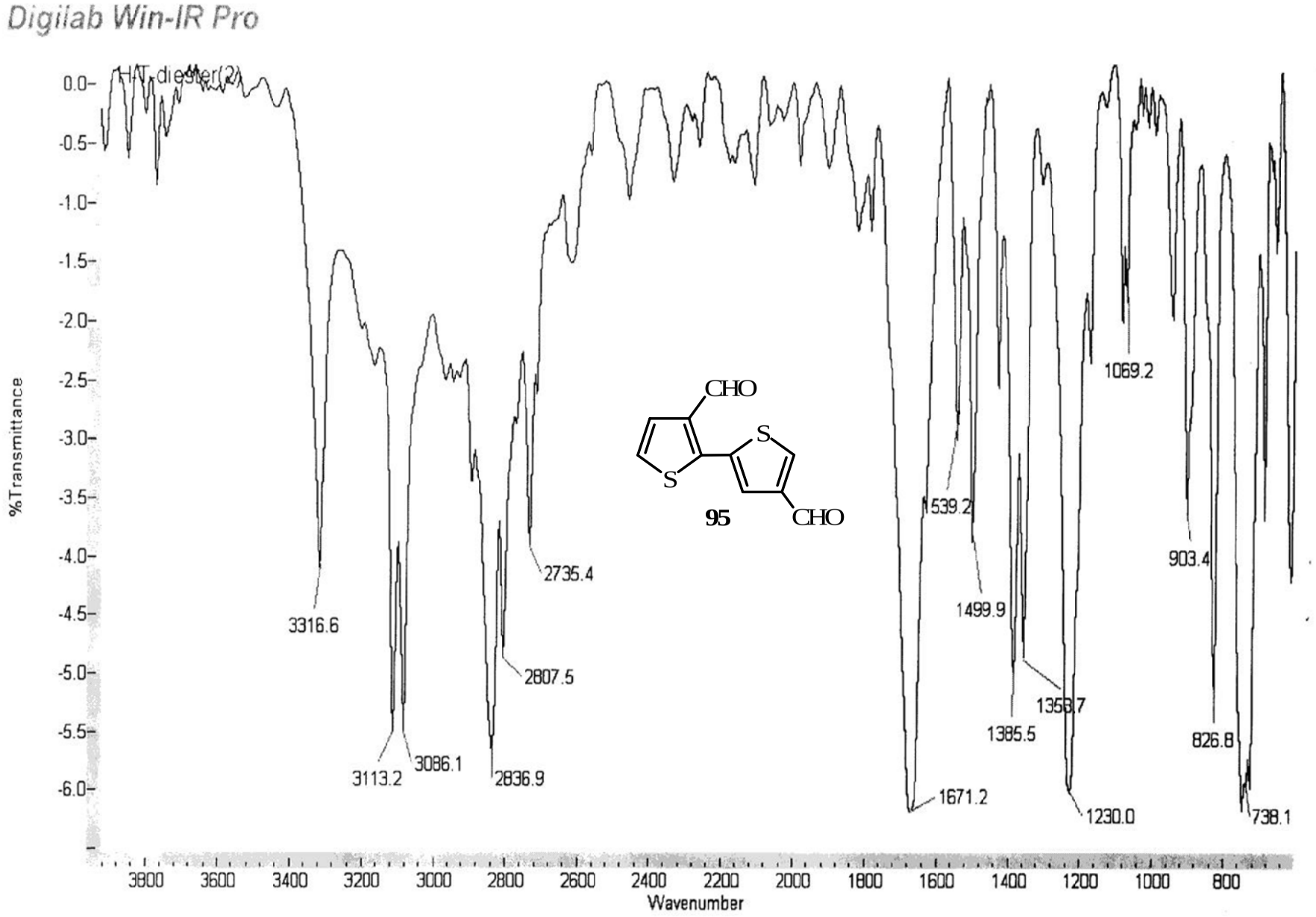
Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 65536
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 2.0840448[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 65536
X_prescans        = 4
X_resolution      = 0.47983613[Hz]
X_sweep           = 31.44654088[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5[ppm]
Clipped           = TRUE
Mod_return        = 1
Scans             = 1217
Total_scans       = 1217

X_90_width        = 14.2[us]
X_acq_time        = 2.0840448[s]
X_angle           = 30[deg]
X_pulse           = 4.73333333[us]
Initial_wait      = 1[s]
Noe_time          = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 30
Relaxation_delay  = 2[s]
Temp_get          = 28.2[dC]
Unblank_time      = 2[us]
```

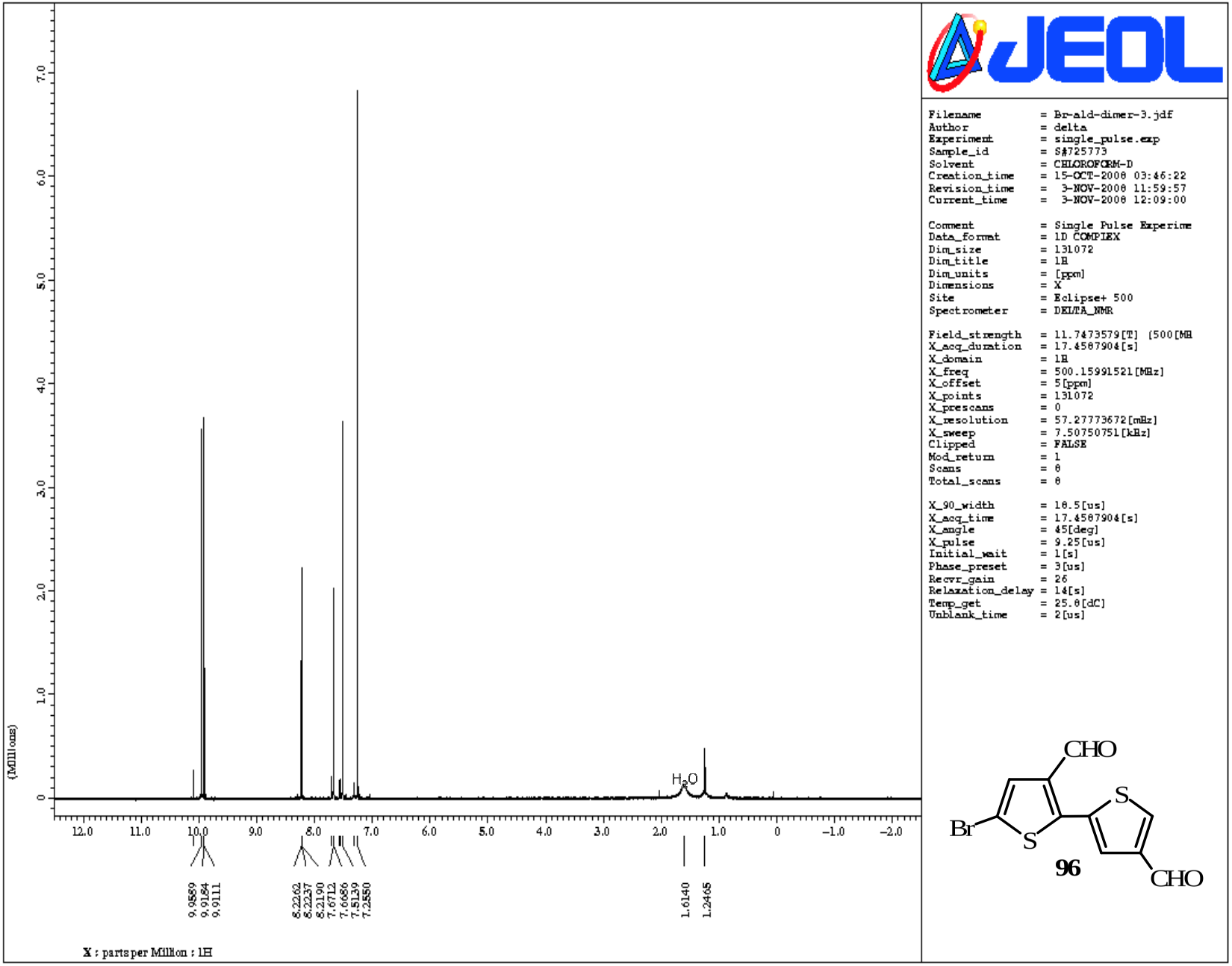


95


Digilab Win-IR Pro
HT diester(2)
%Transmittance
0.0
-0.5
-1.0
-1.5
-2.0
-2.5
-3.0
-3.5
-4.0
-4.5
-5.0
-5.5
-6.0
3316.6
3113.2
3086.1
2836.9
2807.5
2735.4
1671.2
1539.2
1499.9
1385.5
1358.7
1230.0
1069.2
903.4
826.8
738.1
CHO
S
S
CHO
95
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
Wavenumber

APPENDIX 14

^{1}H, ^{13}C NMR and IR spectra of 5-bromo-2,2'-bithiophene-3,4'-dicarbaldehyde (**96**)



JEOL

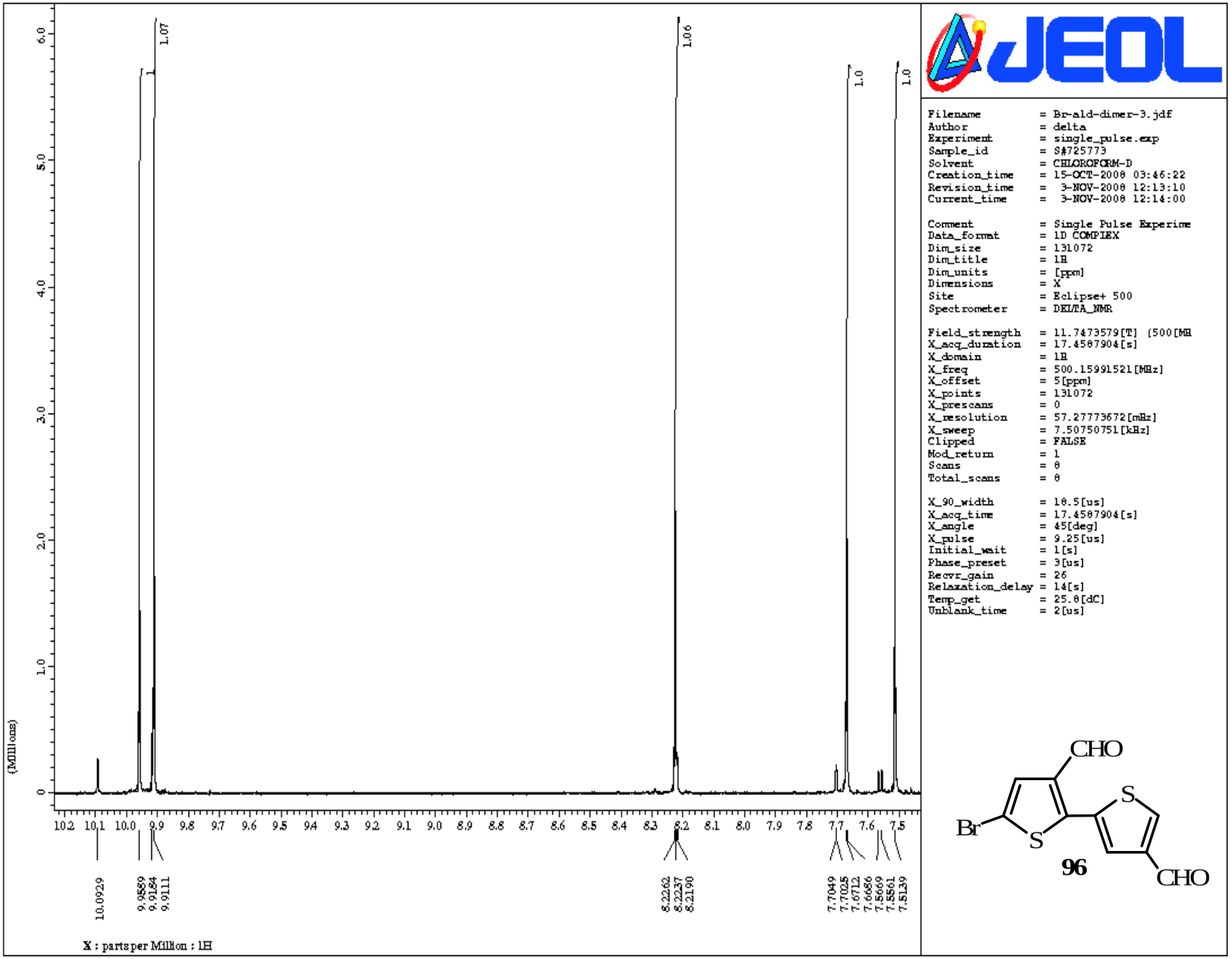
```
Filename          = Br-ald-dimer-3.jdf
Author            = delta
Experiment        = single_pulse.exp
Sample_id         = S#725773
Solvent           = CHLOROFORM-D
Creation_time     = 15-OCT-2008 03:46:22
Revision_time     =  3-NOV-2008 11:59:57
Current_time      =  3-NOV-2008 12:09:00

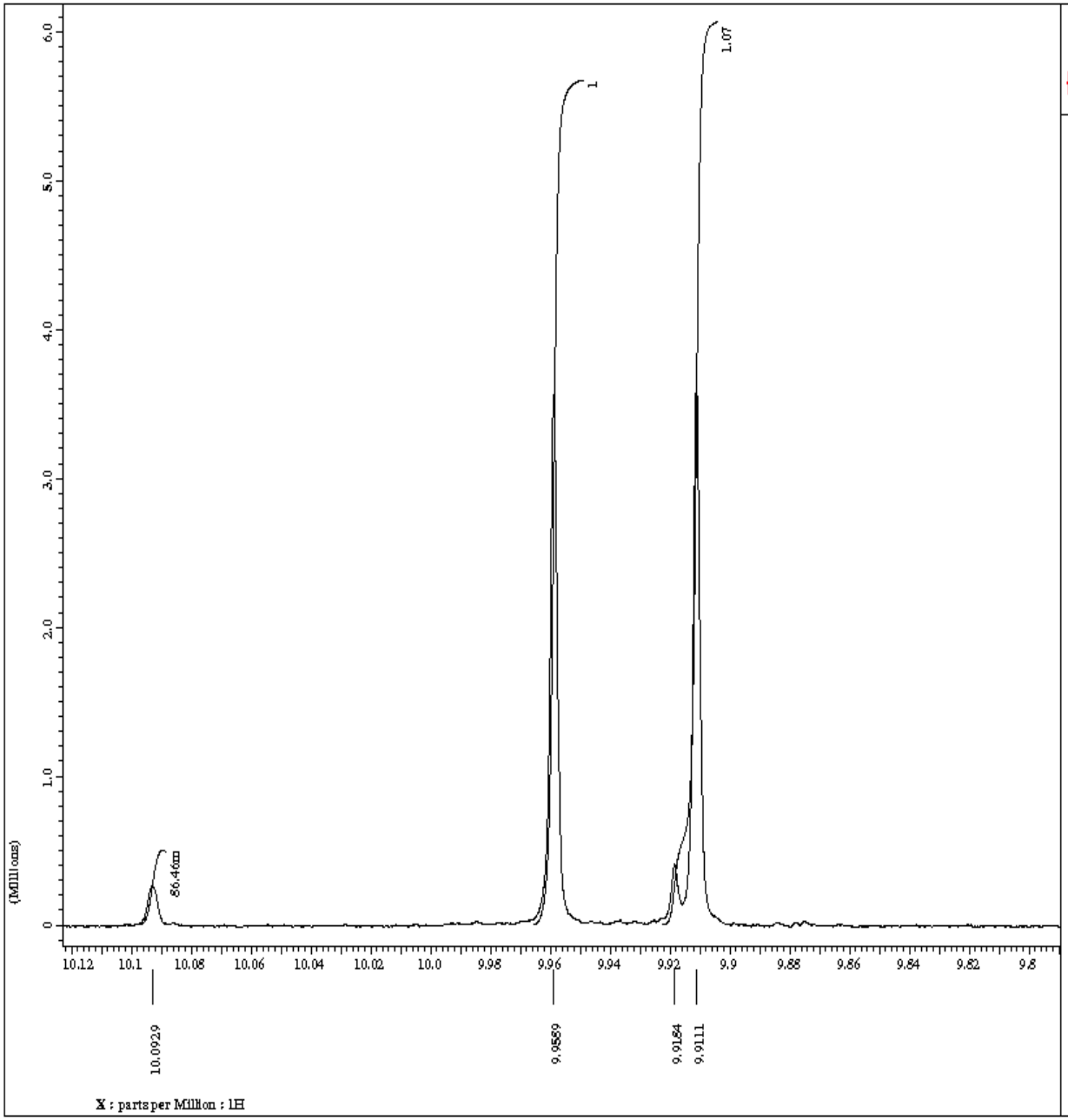
Comment           = Single Pulse Experime
Data_format       = 1D COMPLEX
Dim_size          = 131072
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

Field_strength    = 11.7473579[T]  (500[MH
X_acq_duration    = 17.4587904[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 5[ppm]
X_points          = 131072
X_prescans        = 0
X_resolution      = 57.27773672[mHz]
X_sweep           = 7.50750751[kHz]
Clipped           = FALSE
Mod_return        = 1
Scans             = 8
Total_scans       = 8

X_90_width        = 18.5[us]
X_acq_time        = 17.4587904[s]
X_angle           = 45[deg]
X_pulse           = 9.25[us]
Initial_wait      = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 26
Relaxation_delay  = 14[s]
Temp_get          = 25.8[dC]
Unblank_time      = 2[us]
```


96


1.07
1.06
1.0
1.0
(Millions)
10.0929
9.9589
9.9184
9.9111
8.2262
8.2237
8.2190
7.7049
7.7025
7.6712
7.6686
7.5669
7.5561
7.5139
X : parts per Million : 1H
Filename = Br-ald-dimer-3.jdf
Author = delta
Experiment = single_pulse.exp
Sample_id = S#725773
Solvent = CHLOROFORM-D
Creation_time = 15-OCT-2008 03:46:22
Revision_time = 3-NOV-2008 12:13:10
Current_time = 3-NOV-2008 12:14:00
Comment = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 131072
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 17.458790&[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 131072
X_prescans = 0
X_resolution = 57.27773672[mHz]
X_sweep = 7.50750751[kHz]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 10.5[us]
X_acq_time = 17.458790&[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 26
Relaxation_delay = 14[s]
Temp_get = 25.8[dC]
Unblank_time = 2[us]
CHO
S
Br
S
CHO
96



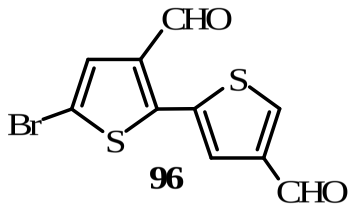
JEOL

```
Filename          = Br-ald-dimer-3.jdf
Author            = delta
Experiment        = single_pulse.exp
Sample_id         = S#725773
Solvent           = CHLOROFORM-D
Creation_time     = 15-OCT-2008 03:46:22
Revision_time     =  3-NOV-2008 12:16:27
Current_time      =  3-NOV-2008 12:16:52

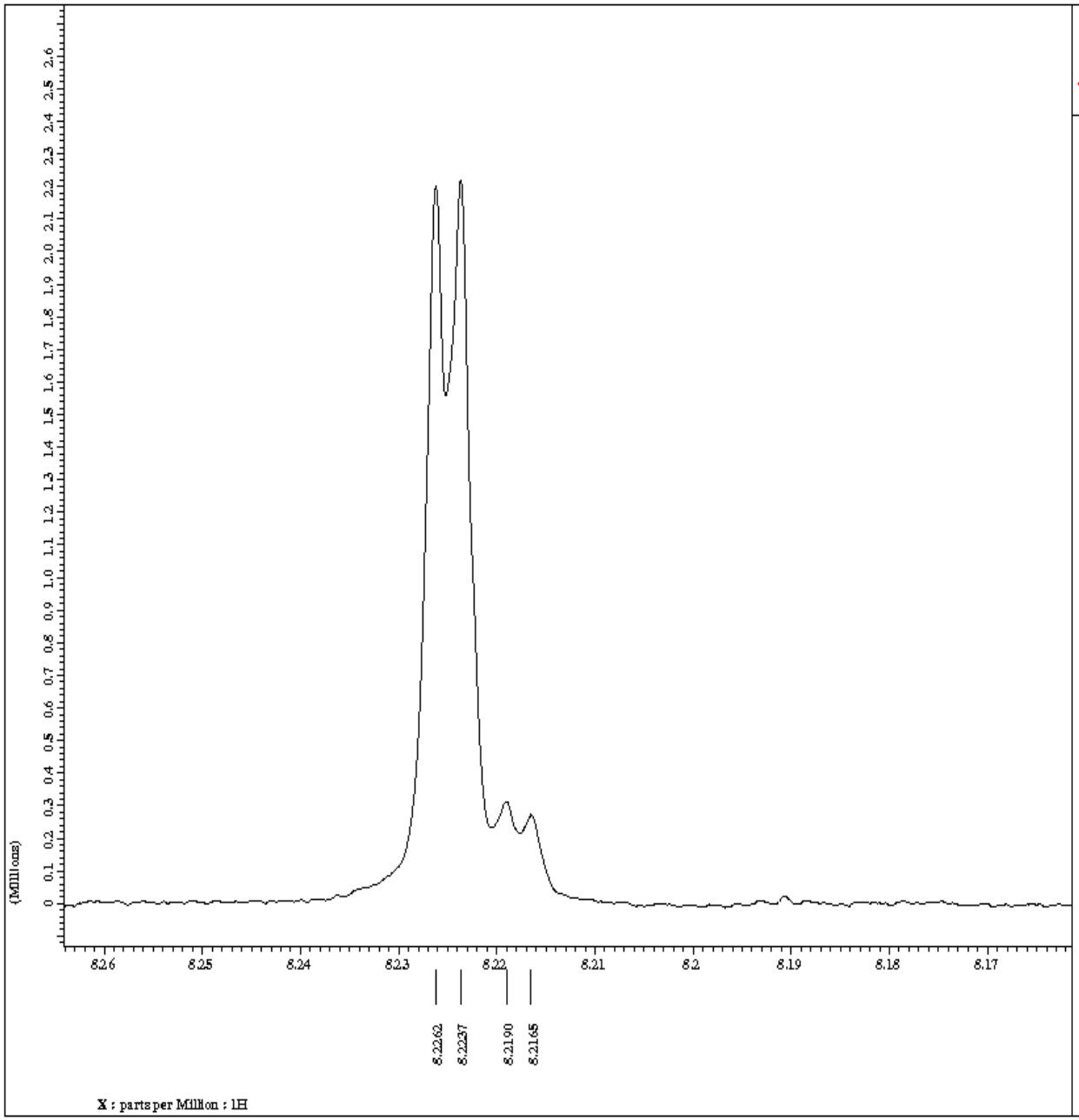
Comment           = Single Pulse Experime
Data_format       = 1D COMPLEX
Dim_size          = 131072
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 17.4587904[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 5[ppm]
X_points          = 131072
X_prescans        = 0
X_resolution      = 57.27773672[mHz]
X_sweep           = 7.50750751[kHz]
Clipped           = FALSE
Mod_return        = 1
Scans             = 8
Total_scans       = 8

X_90_width        = 10.5[us]
X_acq_time        = 17.4587904[s]
X_angle           = 45[deg]
X_pulse           = 9.25[us]
Initial_wait      = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 26
Relaxation_delay  = 14[s]
Temp_get          = 25.8[dC]
Unblank_time      = 2[us]
```



96



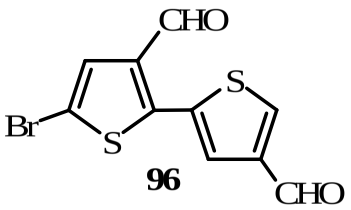
JEOL

```
Filename          = Br-ald-dimer-3.jdf
Author            = delta
Experiment        = single_pulse.exp
Sample_id         = S#725773
Solvent           = CHLOROFORM-D
Creation_time     = 15-OCT-2008 03:46:22
Revision_time     =  3-NOV-2008 12:19:04
Current_time      =  3-NOV-2008 12:19:39

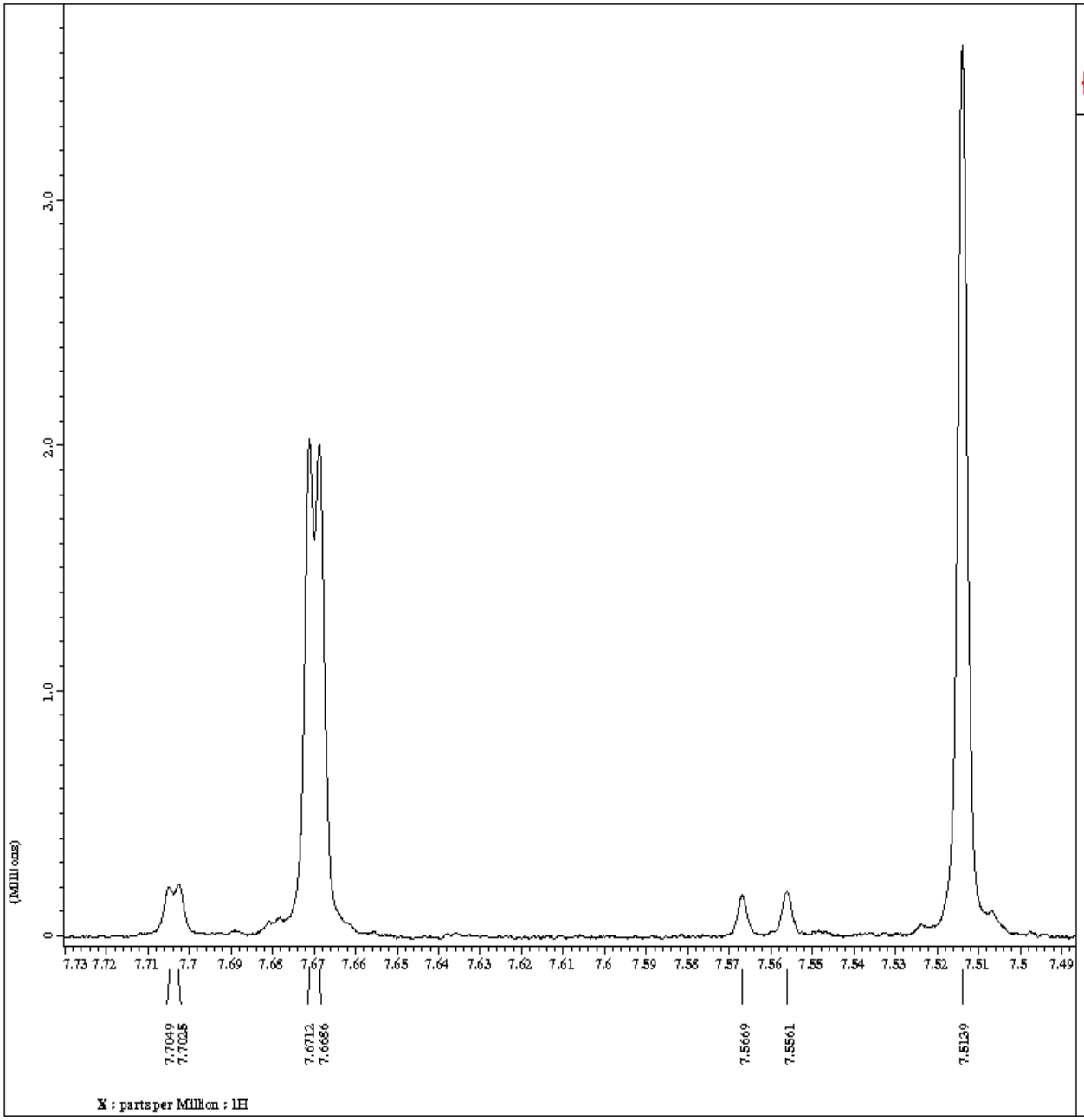
Comment           = Single Pulse Experime
Data_format       = 1D COMPLEX
Dim_size          = 131072
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 17.4587904[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 5[ppm]
X_points          = 131072
X_prescans        = 0
X_resolution      = 57.27773672[mHz]
X_sweep           = 7.50750751[kHz]
Clipped           = FALSE
Mod_return        = 1
Scans             = 8
Total_scans       = 8

X_90_width        = 18.5[us]
X_acq_time        = 17.4587904[s]
X_angle           = 45[deg]
X_pulse           = 9.25[us]
Initial_wait      = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 26
Relaxation_delay  = 14[s]
Temp_get          = 25.8[dC]
Unblank_time      = 2[us]
```



96



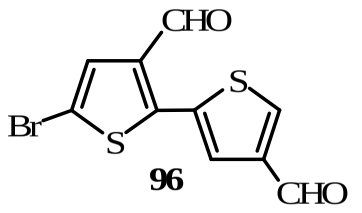
JEOL

```
Filename          = Br-ald-dimer-3.jdf
Author            = delta
Experiment        = single_pulse.exp
Sample_id         = S#725773
Solvent           = CHLOROFORM-D
Creation_time     = 15-OCT-2008 03:46:22
Revision_time     =  3-NOV-2008 12:19:04
Current_time      =  3-NOV-2008 12:22:07

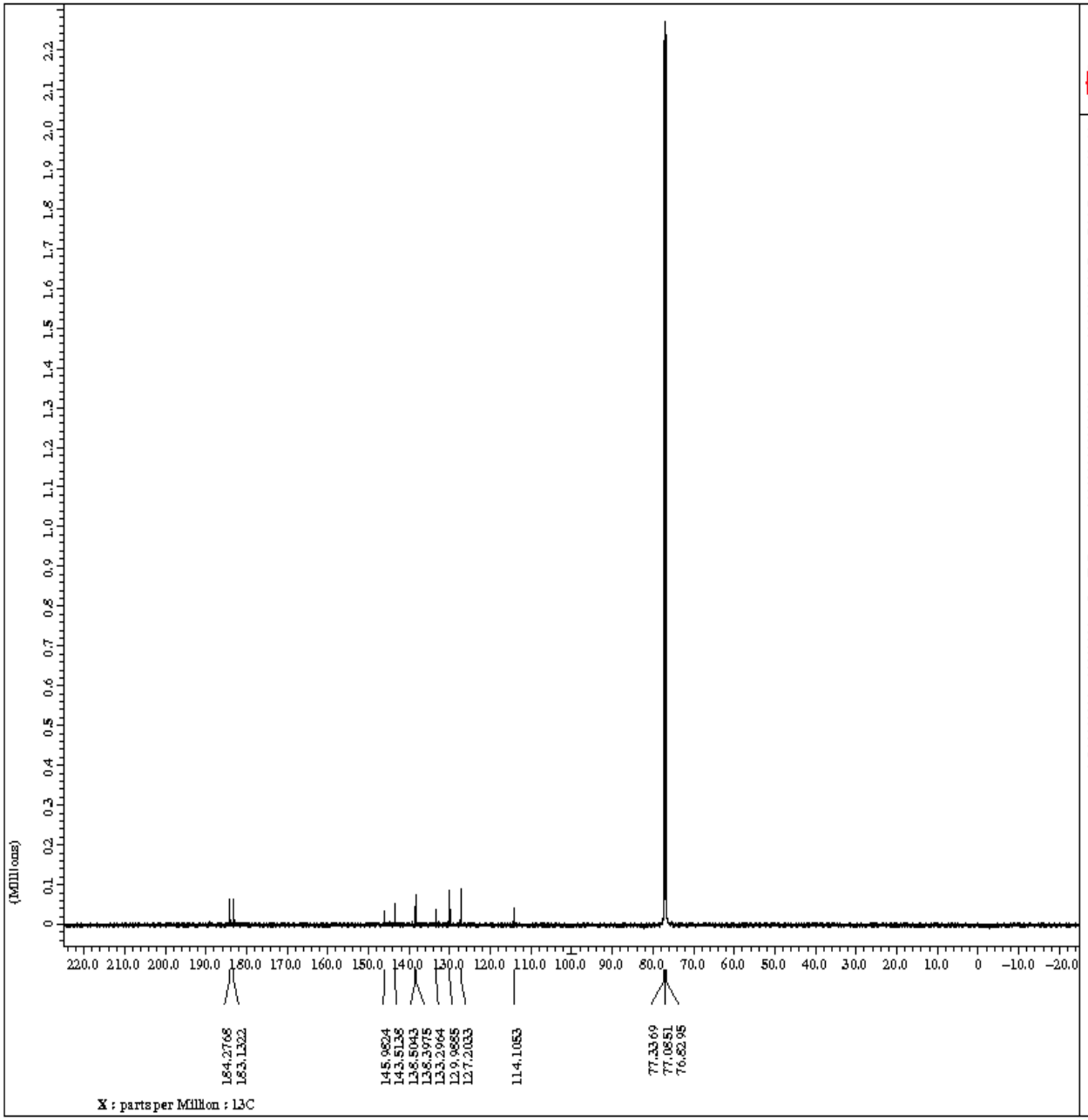
Comment           = Single Pulse Experime
Data_format       = 1D COMPLEX
Dim_size          = 131072
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 17.4587904[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 5[ppm]
X_points          = 131072
X_prescans        = 0
X_resolution      = 57.27773672[mHz]
X_sweep           = 7.50750751[kHz]
Clipped           = FALSE
Mod_return        = 1
Scans             = 8
Total_scans       = 8

X_90_width        = 10.5[us]
X_acq_time        = 17.4587904[s]
X_angle           = 45[deg]
X_pulse           = 9.25[us]
Initial_wait      = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 26
Relaxation_delay  = 14[s]
Temp_get          = 25.8[dC]
Unblank_time      = 2[us]
```

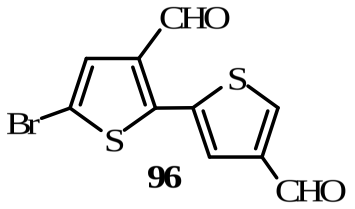


96

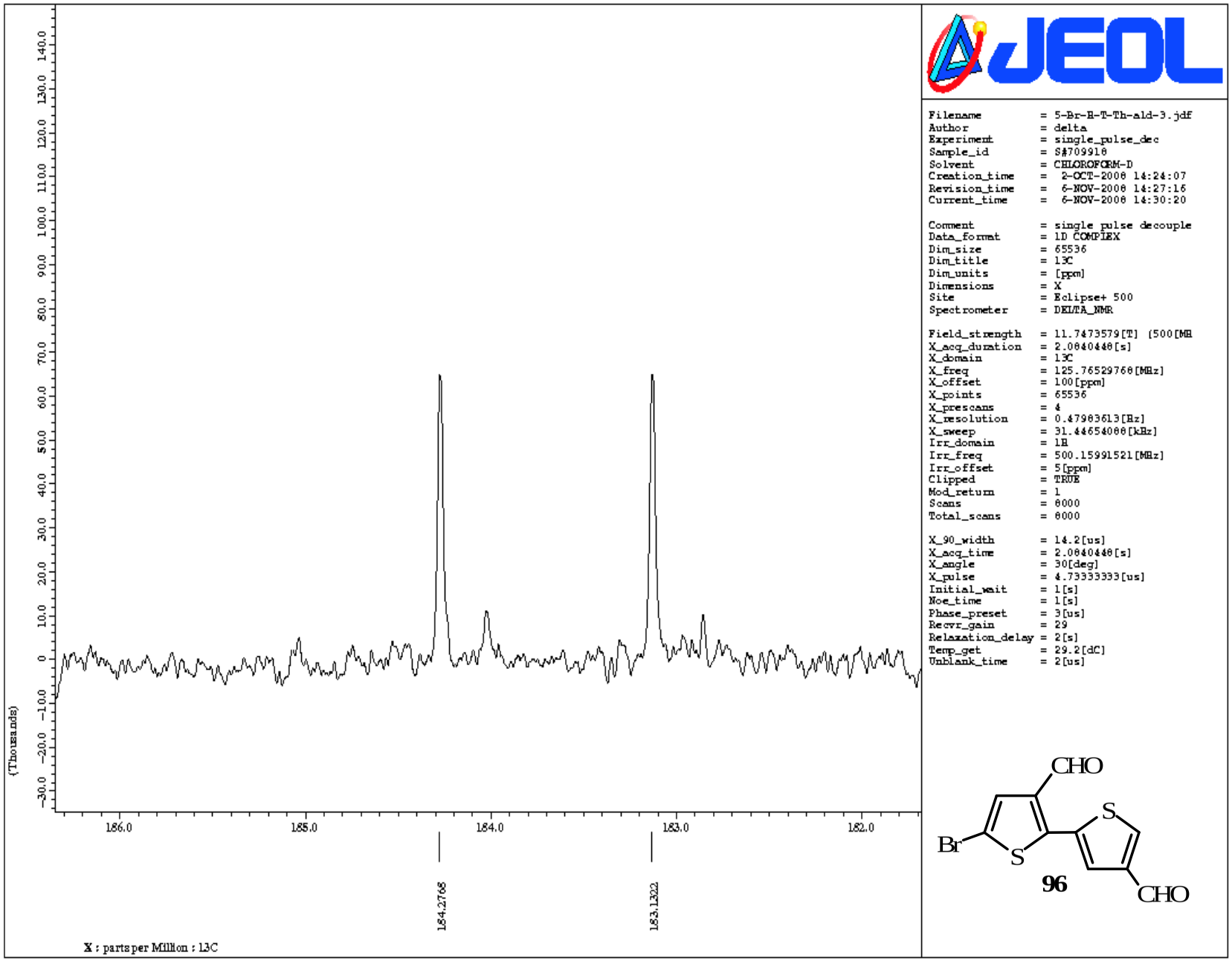


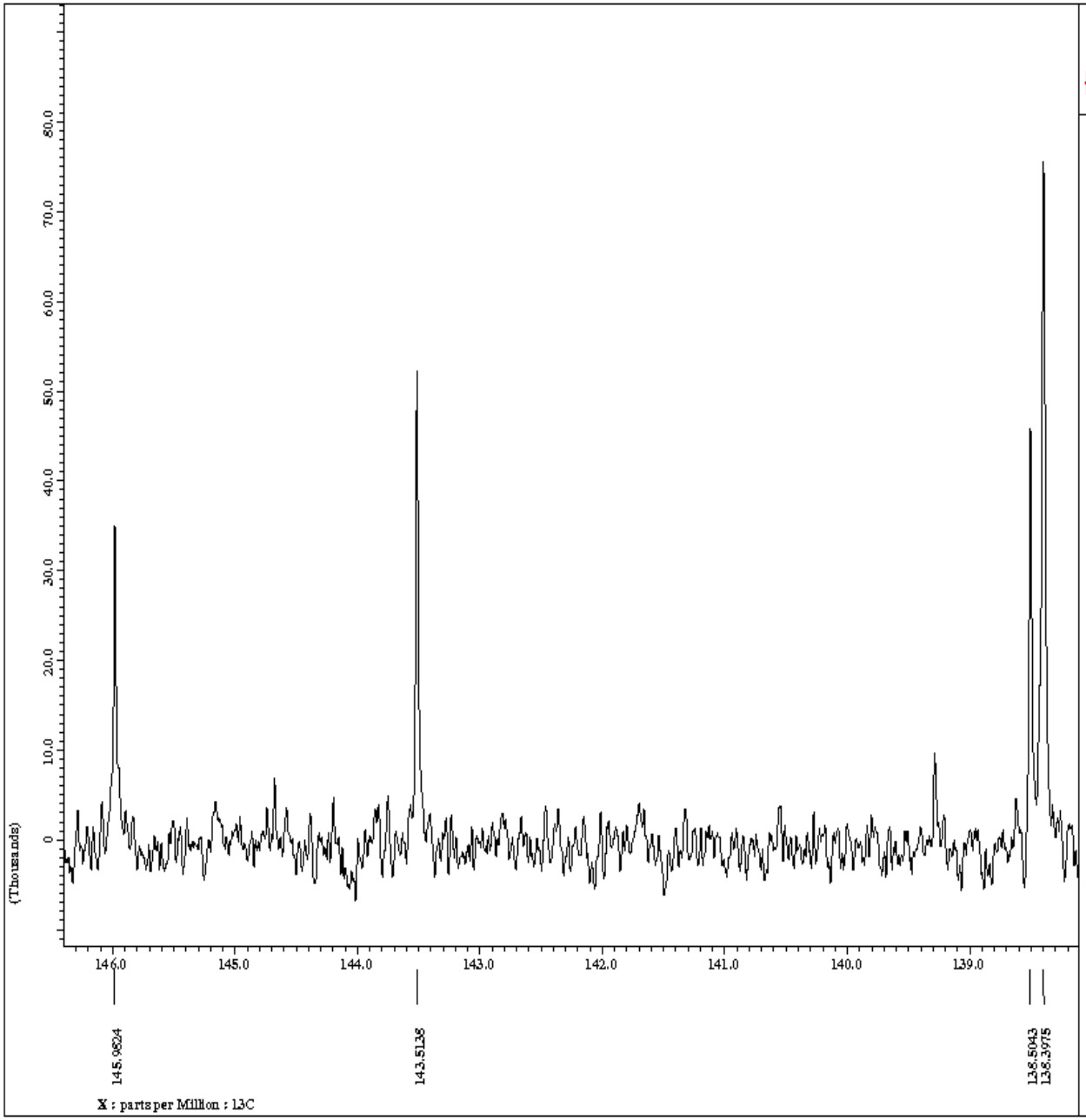
JEOL

Filename	=	5-Br-H-T-Th-ald-3.jdf
Author	=	delta
Experiment	=	single_pulse_dec
Sample_id	=	S#709910
Solvent	=	CHLOROFORM-D
Creation_time	=	2-OCT-2008 14:24:07
Revision_time	=	6-NOV-2008 14:27:16
Current_time	=	6-NOV-2008 14:27:49
Comment	=	single_pulse decouple
Data_format	=	1D COMPLEX
Dim_size	=	65536
Dim_title	=	13C
Dim_units	=	[ppm]
Dimensions	=	X
Site	=	Eclipse+ 500
Spectrometer	=	DELTA_NMR
Field_strength	=	11.7473579[T] (500[MH
X_acq_duration	=	2.0840448[s]
X_domain	=	13C
X_freq	=	125.76529768[MHz]
X_offset	=	100[ppm]
X_points	=	65536
X_prescans	=	4
X_resolution	=	0.47983613[Hz]
X_sweep	=	31.44654088[kHz]
Irr_domain	=	1H
Irr_freq	=	500.15991521[MHz]
Irr_offset	=	5[ppm]
Clipped	=	TRUE
Mod_return	=	1
Scans	=	8000
Total_scans	=	8000
X_90_width	=	14.2[us]
X_acq_time	=	2.0840448[s]
X_angle	=	30[deg]
X_pulse	=	4.73333333[us]
Initial_wait	=	1[s]
Noe_time	=	1[s]
Phase_preset	=	3[us]
Recvr_gain	=	29
Relaxation_delay	=	2[s]
Temp_get	=	29.2[dC]
Unblank_time	=	2[us]



96


(Thousands)
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
-30.0
186.0
185.0
184.0
183.0
182.0
184.2768
183.1322
X : parts per Million : 13C
JEOL
Filename = 5-Br-B-T-Th-ald-3.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = S#709910
Solvent = CHLOROFORM-D
Creation_time = 2-OCT-2008 14:24:07
Revision_time = 6-NOV-2008 14:27:16
Current_time = 6-NOV-2008 14:30:20
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 65536
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.0840448[s]
X_domain = 13C
X_freq = 125.76529768[MHz]
X_offset = 100[ppm]
X_points = 65536
X_prescans = 4
X_resolution = 0.4798361 3[Hz]
X_sweep = 31.44654088[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5[ppm]
Clipped = TRUE
Mod_return = 1
Scans = 8000
Total_scans = 8000
X_90_width = 14.2[us]
X_acq_time = 2.0840448[s]
X_angle = 30[deg]
X_pulse = 4.73333333[us]
Initial_wait = 1[s]
Noe_time = 1[s]
Phase_preset = 3[us]
Recvr_gain = 29
Relaxation_delay = 2[s]
Temp_get = 29.2[dC]
Unblank_time = 2[us]
CHO
S
Br
S
CHO
96



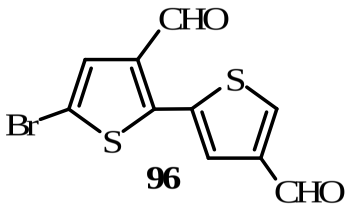
JEOL

```
Filename          = 5-Br-B-T-Th-ald-3.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#709918
Solvent           = CHLOROFORM-D
Creation_time     =  2-OCT-2008 14:24:07
Revision_time     =  6-NOV-2008 14:27:16
Current_time      =  6-NOV-2008 14:32:37

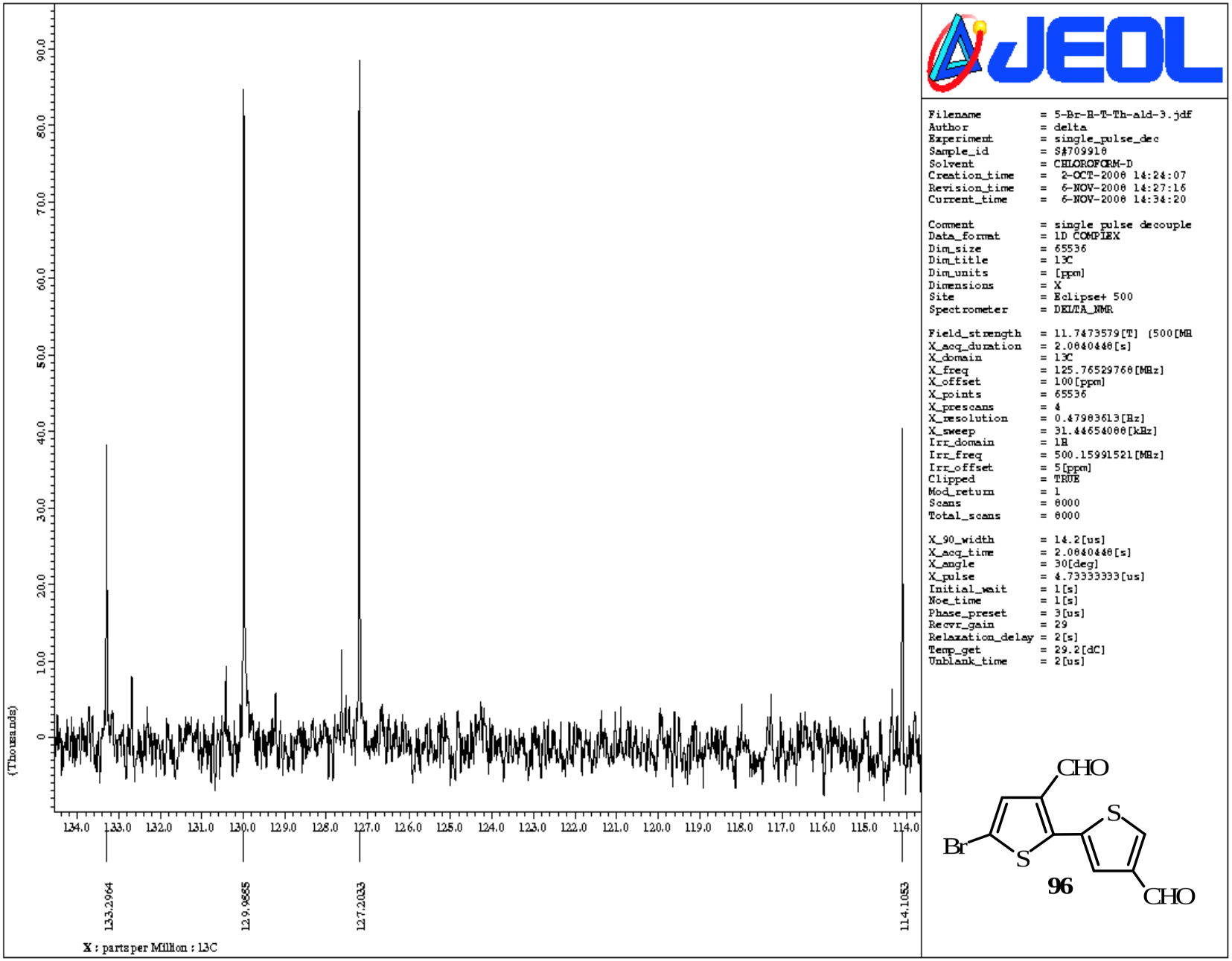
Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 65536
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

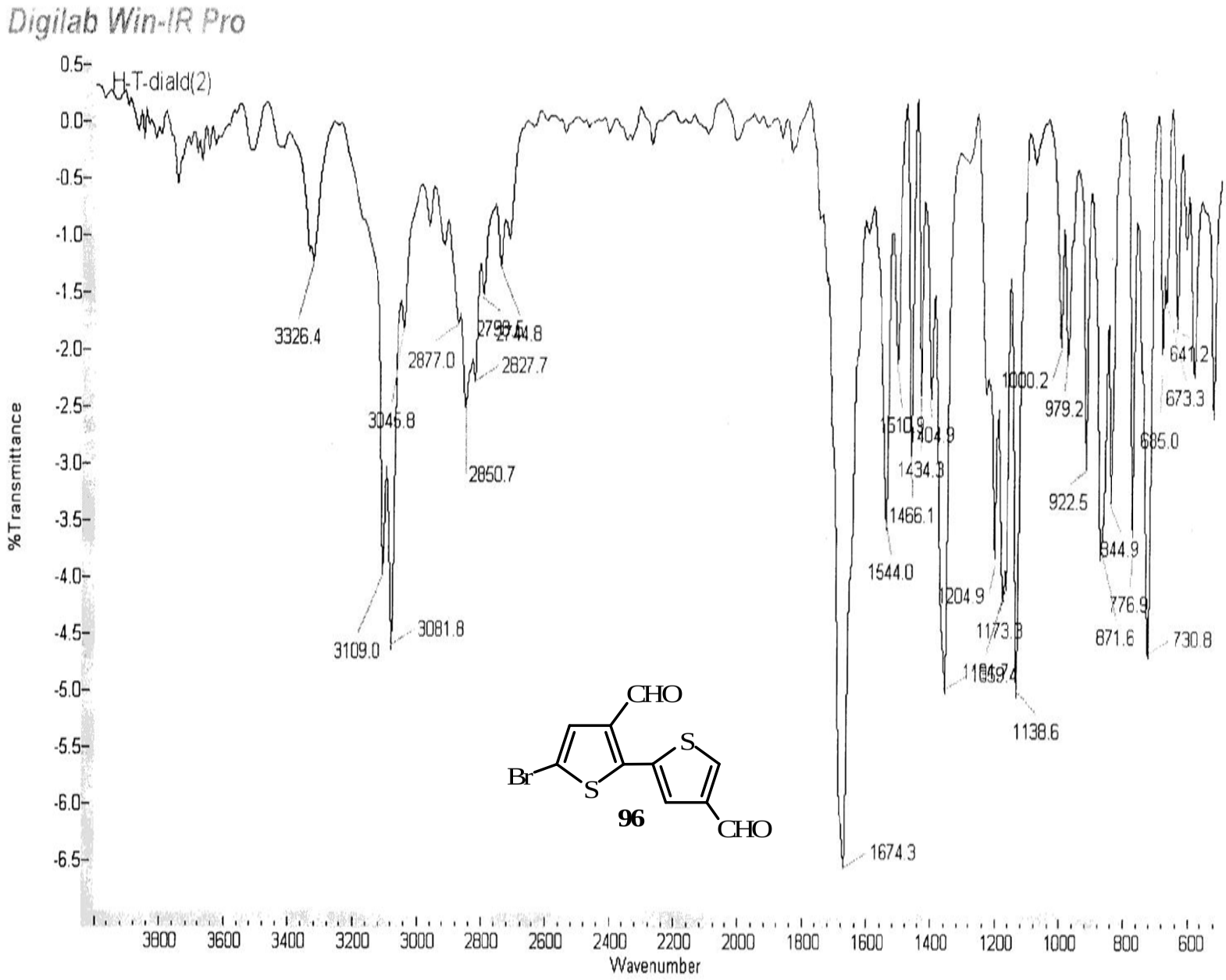
Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 2.0840448[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 65536
X_prescans        = 4
X_resolution      = 0.47983613[Hz]
X_sweep           = 31.44654088[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5[ppm]
Clipped           = TRUE
Mod_return        = 1
Scans             = 8000
Total_scans       = 8000

X_90_width        = 14.2[us]
X_acq_time        = 2.0840448[s]
X_angle           = 30[deg]
X_pulse           = 4.73333333[us]
Initial_wait      = 1[s]
Noe_time          = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 29
Relaxation_delay  = 2[s]
Temp_get          = 29.2[dC]
Unblank_time      = 2[us]
```



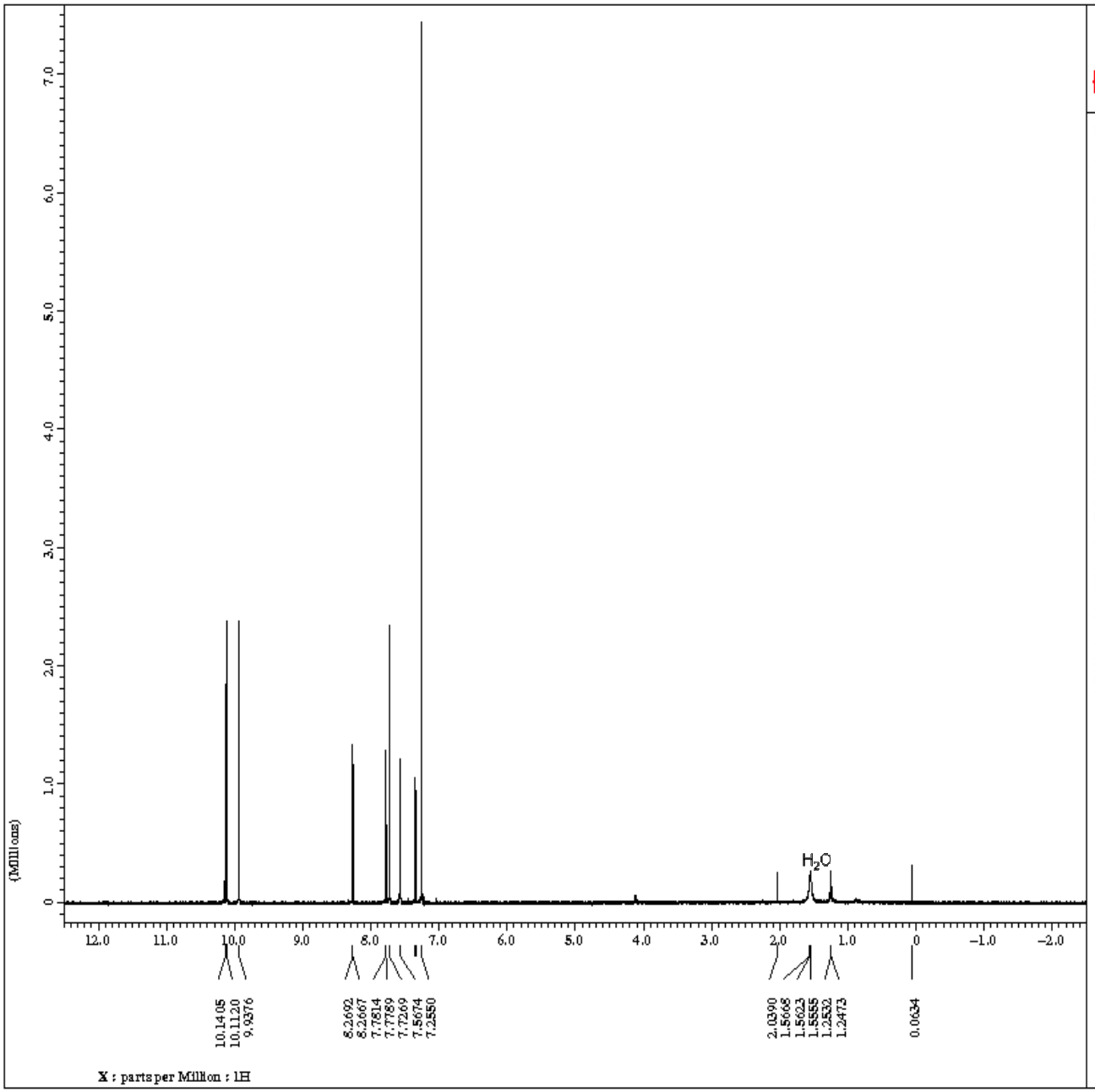
96

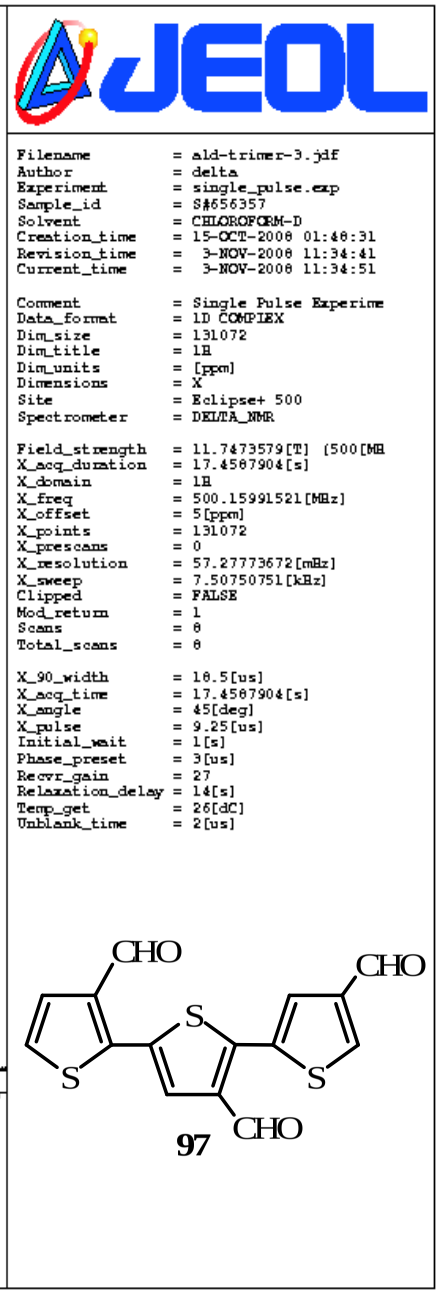

(Thousands)
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
134.0 133.0 132.0 131.0 130.0 129.0 128.0 127.0 126.0 125.0 124.0 123.0 122.0 121.0 120.0 119.0 118.0 117.0 116.0 115.0 114.0
133.2964
129.9885
127.2033
114.1053
X : parts per Million : 13C
Filename = 5-Br-H-T-Th-ald-3.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = S#709910
Solvent = CHLOROFORM-D
Creation_time = 2-OCT-2008 14:24:07
Revision_time = 6-NOV-2008 14:27:16
Current_time = 6-NOV-2008 14:34:20
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 65536
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.0840448[s]
X_domain = 13C
X_freq = 125.76529768[MHz]
X_offset = 100[ppm]
X_points = 65536
X_prescans = 4
X_resolution = 0.47983613[Hz]
X_sweep = 31.44654088[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5[ppm]
Clipped = TRUE
Mod_return = 1
Scans = 8000
Total_scans = 8000
X_90_width = 14.2[us]
X_acq_time = 2.0840448[s]
X_angle = 30[deg]
X_pulse = 4.73333333[us]
Initial_wait = 1[s]
Noe_time = 1[s]
Phase_preset = 3[us]
Recvr_gain = 29
Relaxation_delay = 2[s]
Temp_get = 29.2[dC]
Unblank_time = 2[us]
CHO
S
Br
S
CHO
96

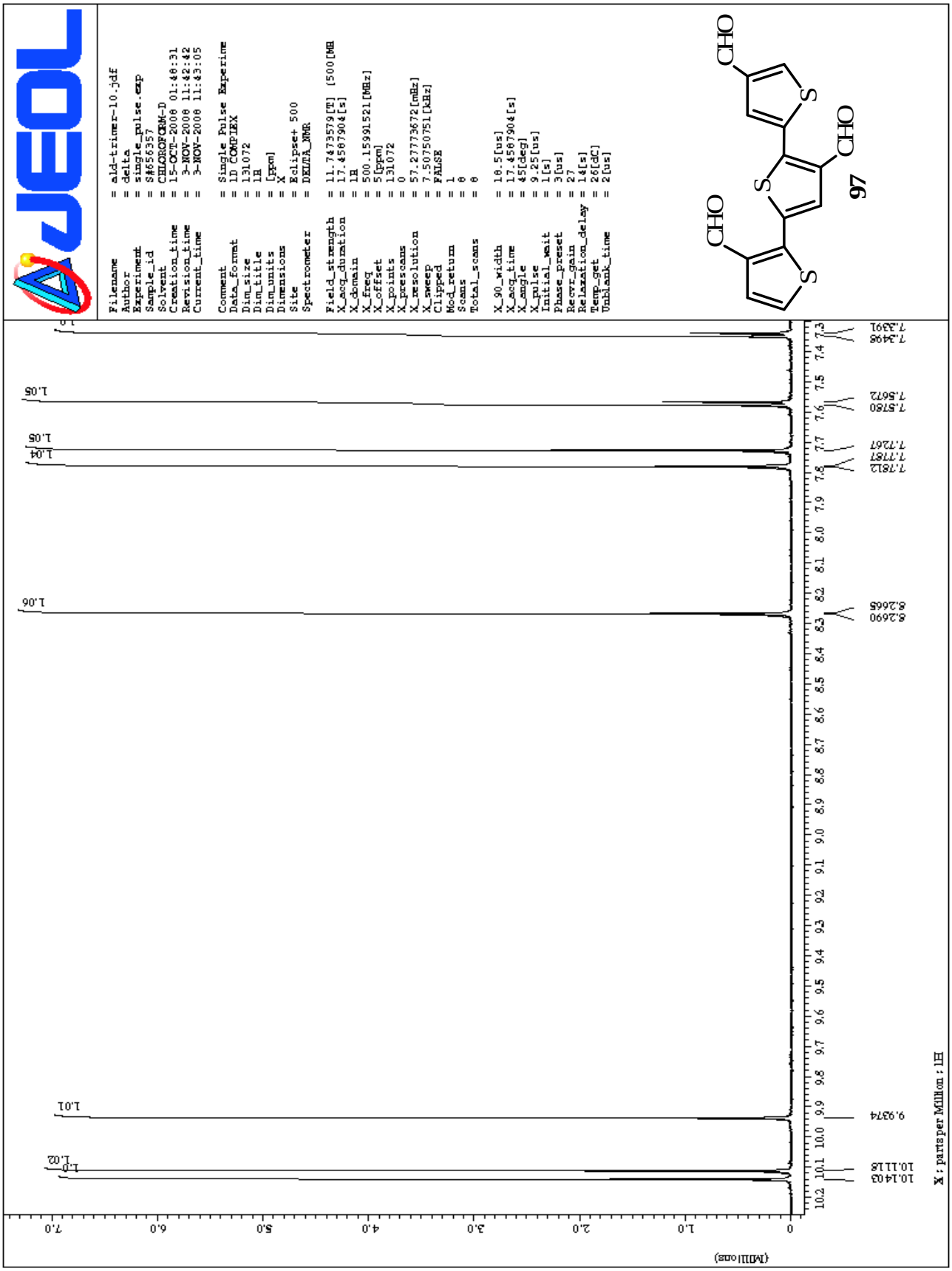

Digilab Win-IR Pro
H-T-diald(2)
%Transmittance
Wavenumber
3326.4
3109.0
3081.8
3045.8
2877.0
2850.7
2827.7
1674.3
1544.0
1466.1
1434.3
1204.9
1138.6
1000.2
979.2
922.5
871.6
776.9
730.8
673.3
685.0
CHO
S
Br
S
CHO
96

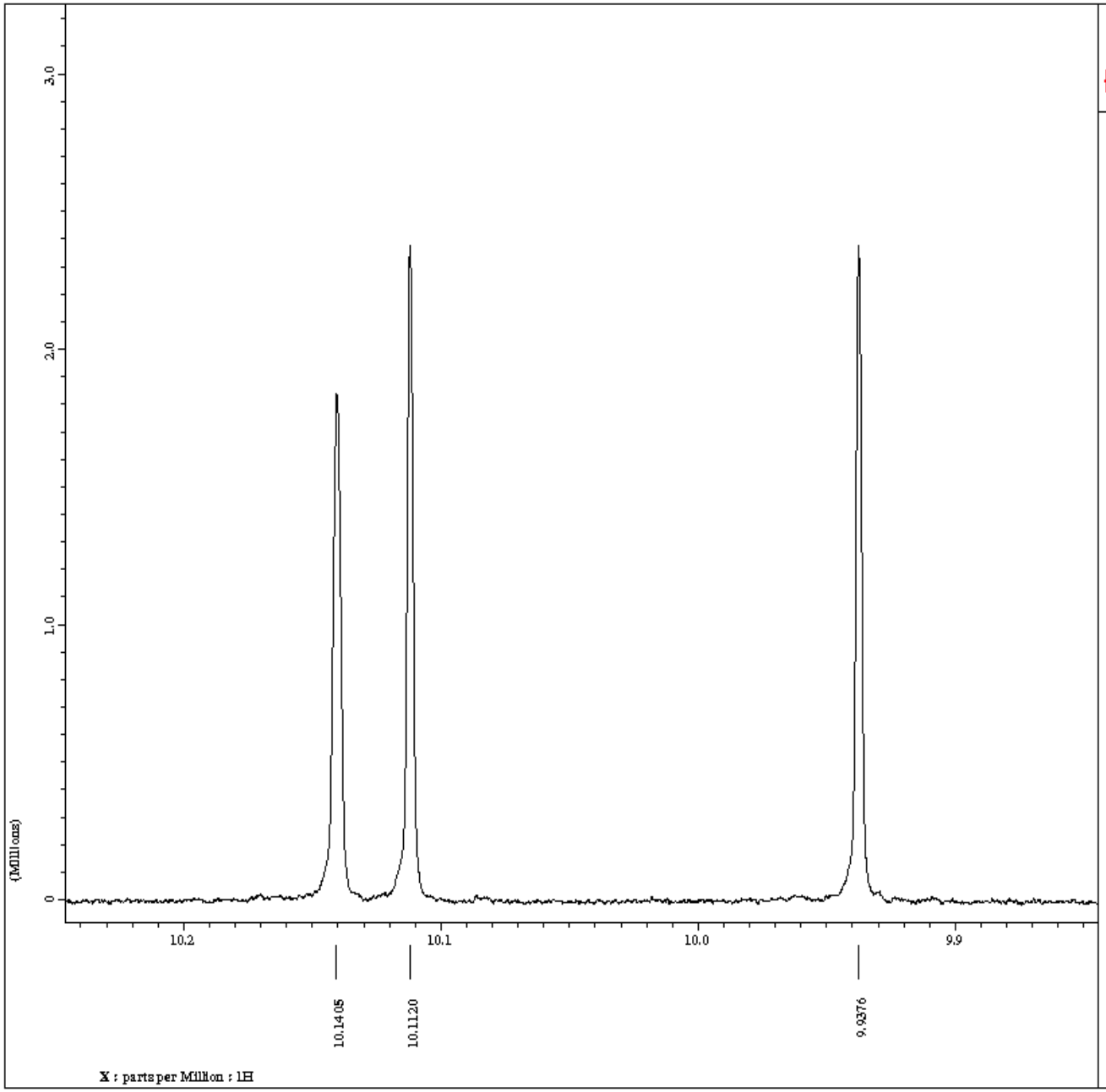
APPENDIX 15

^{1}H, ^{13}C NMR and IR spectra of 3,4',4''-tri-formyl-2,2':5',2''-terthiophene (**97**)


(Millions)
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
−1.0
−2.0
H2O
10.1405
10.1120
9.9376
8.2692
8.2667
7.7814
7.7789
7.7269
7.5674
7.2550
2.0390
1.5668
1.5623
1.5555
1.2532
1.2473
0.0634
X : parts per Million : 1H


JEOL
Filename = ald-trimer-3.jdf
Author = delta
Experiment = single_pulse.exp
Sample_id = S#656357
Solvent = CHLOROFORM-D
Creation_time = 15-OCT-2008 01:48:31
Revision_time = 3-NOV-2008 11:34:41
Current_time = 3-NOV-2008 11:34:51
Comment = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 131072
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 17.4587904[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 131072
X_prescans = 0
X_resolution = 57.27773672[mHz]
X_sweep = 7.50750751[kHz]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 10.5[us]
X_acq_time = 17.4587904[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 27
Relaxation_delay = 14[s]
Temp_get = 26[dC]
Unblank_time = 2[us]
CHO
CHO
S
S
S
CHO
97


JEOL
Filename = ald-trimer-10.jdf
Author = delta
Experiment = single_pulse.exp
Sample_id = S#656357
Solvent = CHLOROFORM-D
Creation_time = 15-OCT-2008 01:40:31
Revision_time = 3-NOV-2008 11:42:42
Current_time = 3-NOV-2008 11:43:05
Comment = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 131072
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 17.4567904[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 131072
X_prescans = 0
X_resolution = 57.27773672[mHz]
X_sweep = 7.50750751[kHz]
Clipped = PAUSE
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 10.5[us]
X_acq_time = 17.4567904[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 27
Relaxation_delay = 14[s]
Temp_get = 26[dC]
Unblank_time = 2[us]
CHO
CHO
CHO
S
S
S
97
1.02
1.00
1.01
1.06
1.04
1.05
1.05
10.1403
10.1118
9.9374
8.2690
8.2665
7.7812
7.7787
7.7267
7.5780
7.5672
7.3498
7.3391
X : parts per Million : 1H
(Million)



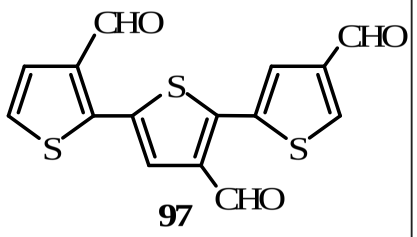
JEOL

```
Filename          = ald-trimer-10.jdf
Author            = delta
Experiment        = single_pulse.exp
Sample_id         = S#656357
Solvent           = CHLOROFORM-D
Creation_time     = 15-OCT-2008 01:48:31
Revision_time     =  3-NOV-2008 11:44:43
Current_time      =  3-NOV-2008 11:45:04

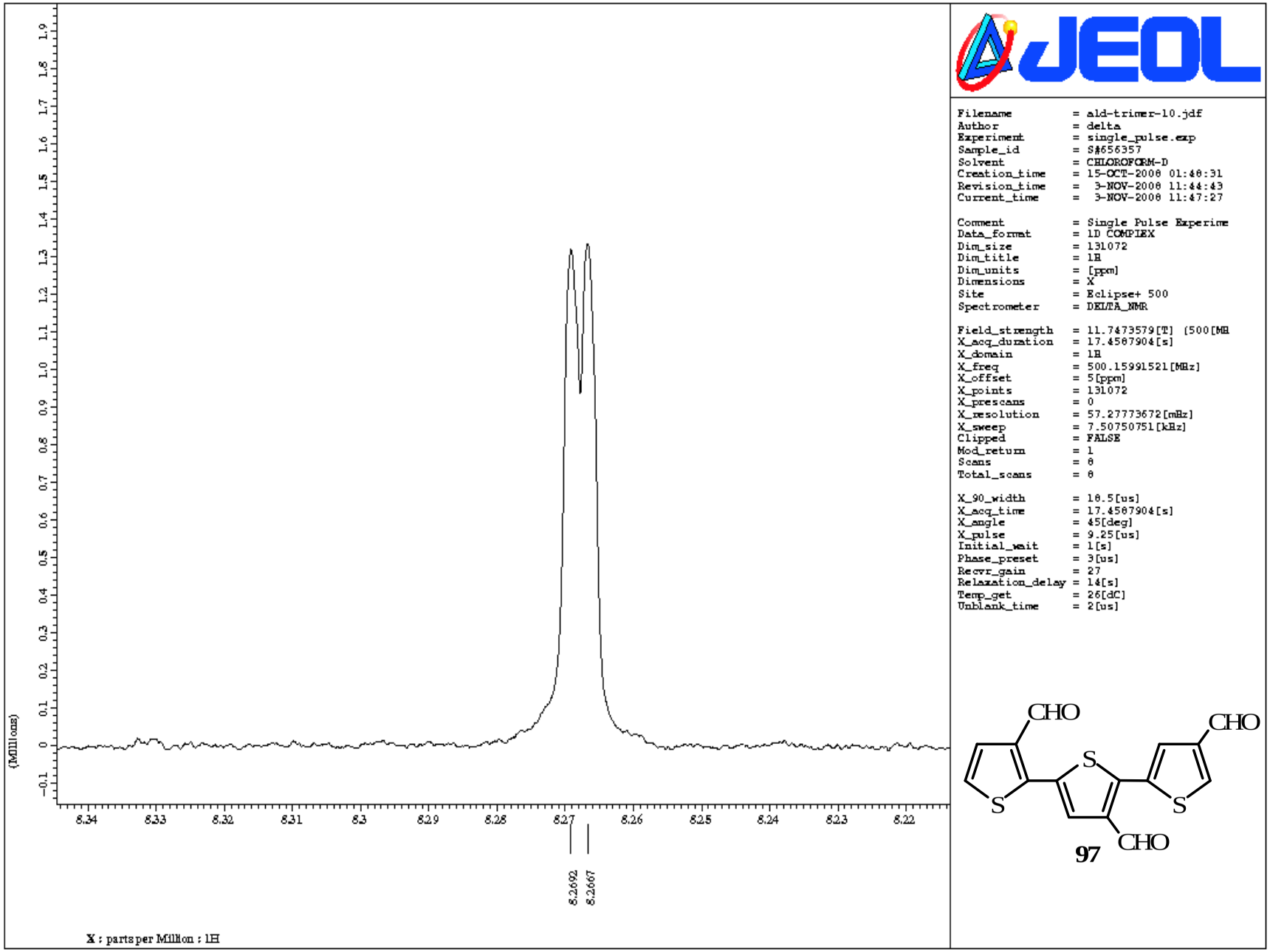
Comment           = Single Pulse Experime
Data_format       = 1D COMPLEX
Dim_size          = 131072
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

Field_strength    = 11.7473579[T]  (500[MH
X_acq_duration    = 17.4567904[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 5[ppm]
X_points          = 131072
X_prescans        = 0
X_resolution      = 57.27773672[mHz]
X_sweep           = 7.50750751[kHz]
Clipped           = FALSE
Mod_return        = 1
Scans             = 8
Total_scans       = 8

X_90_width        = 10.5[us]
X_acq_time        = 17.4567904[s]
X_angle           = 45[deg]
X_pulse           = 9.25[us]
Initial_wait      = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 27
Relaxation_delay  = 14[s]
Temp_get          = 26[dC]
Unblank_time      = 2[us]
```



97



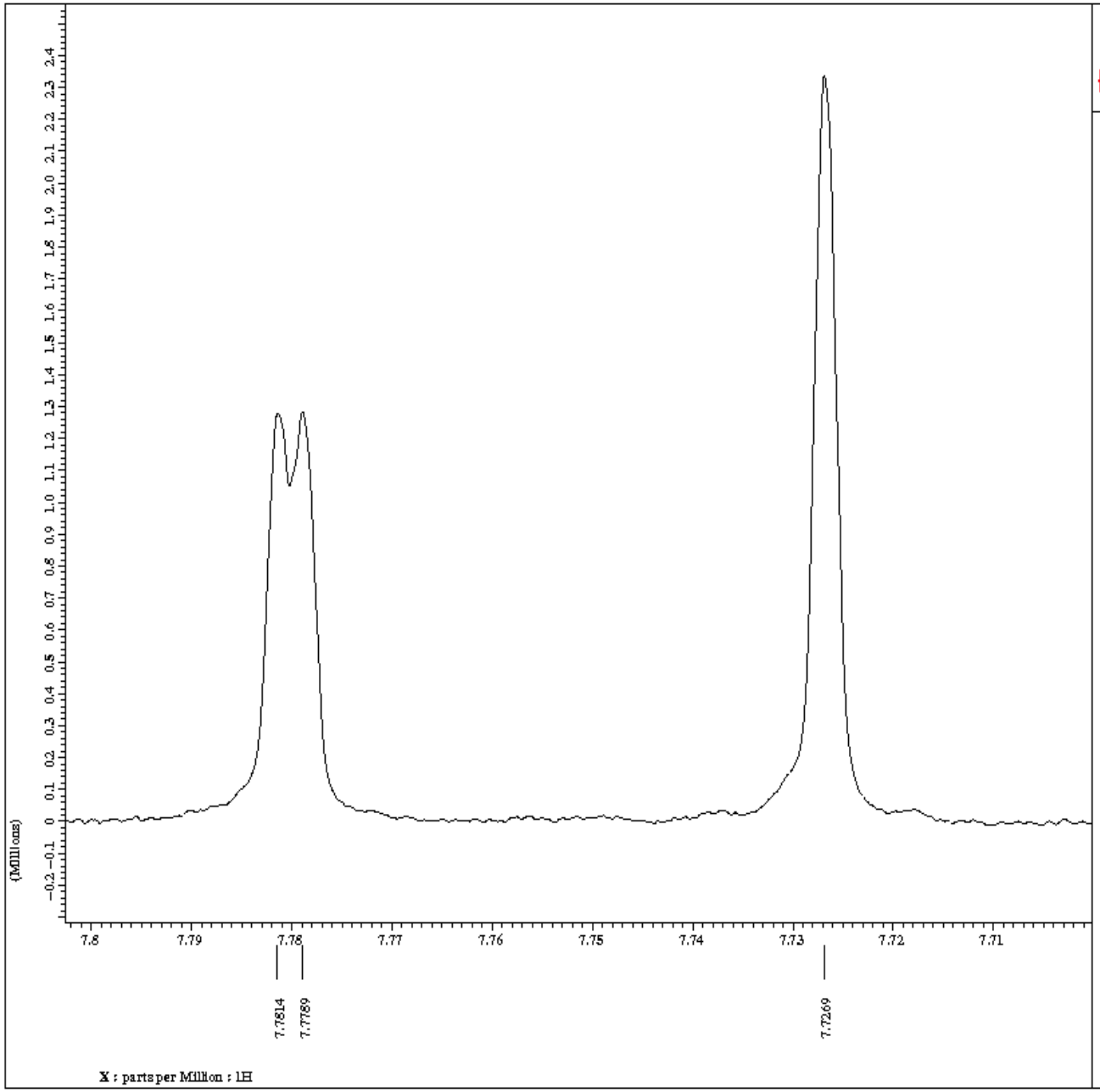
Filename = ald-trimer-10.jdf
Author = delta
Experiment = single_pulse.exp
Sample_id = S#656357
Solvent = CHLOROFORM-D
Creation_time = 15-OCT-2008 01:40:31
Revision_time = 3-NOV-2008 11:44:43
Current_time = 3-NOV-2008 11:47:27

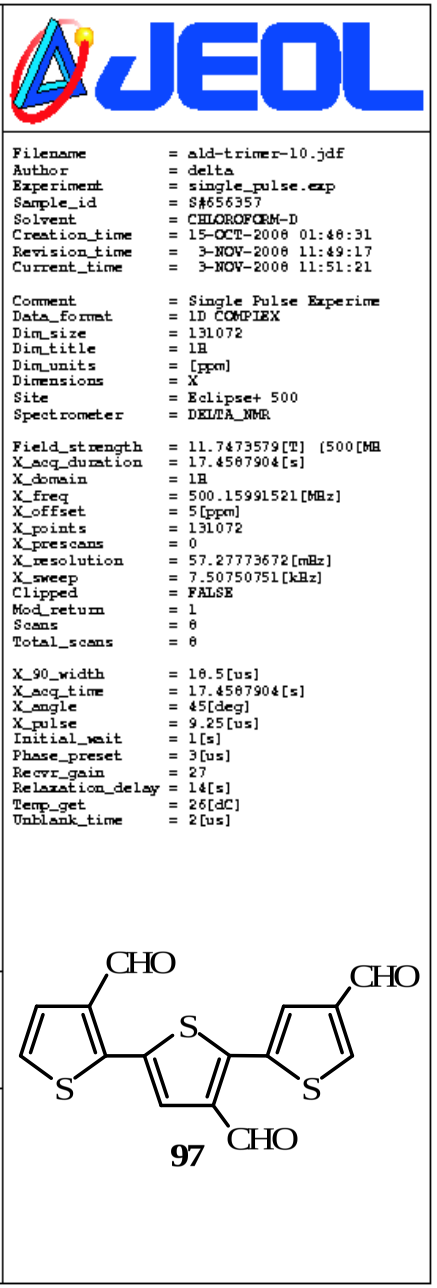
Comment = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 131072
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR

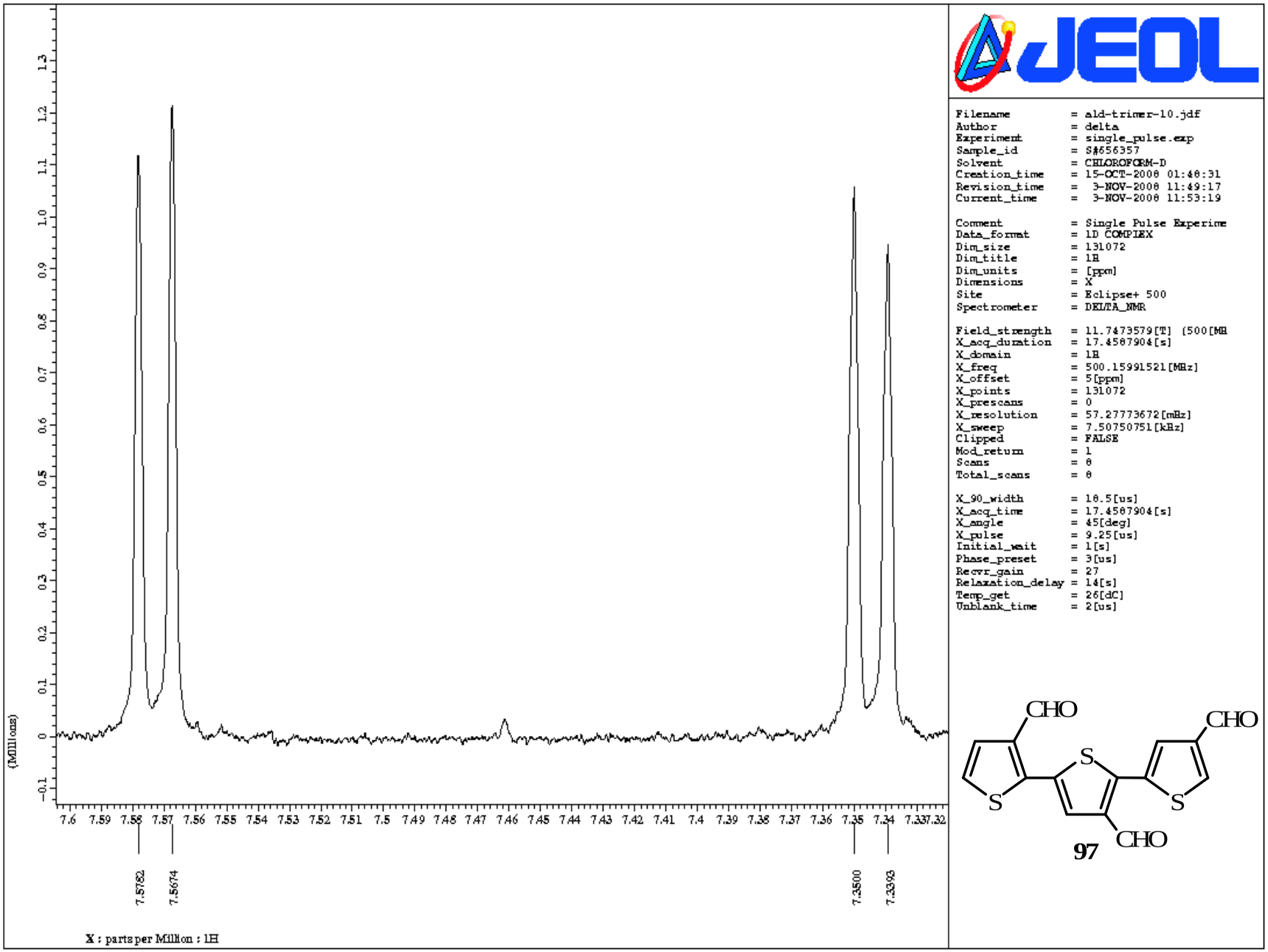
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 17.4587904[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 131072
X_prescans = 0
X_resolution = 57.27773672[mHz]
X_sweep = 7.50750751[kHz]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8

X_90_width = 18.5[us]
X_acq_time = 17.4587904[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 27
Relaxation_delay = 14[s]
Temp_get = 26[dC]
Unblank_time = 2[us]

97


(Millions)
2.4
2.3
2.2
2.1
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
−0.1
−0.2
7.8
7.79
7.78
7.77
7.76
7.75
7.74
7.73
7.72
7.71
7.7814
7.7789
7.7269
X : parts per Million : 1H


JEOL
Filename = ald-trimer-10.jdf
Author = delta
Experiment = single_pulse.exp
Sample_id = S#656357
Solvent = CHLOROFORM-D
Creation_time = 15-OCT-2008 01:48:31
Revision_time = 3-NOV-2008 11:49:17
Current_time = 3-NOV-2008 11:51:21
Comment = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 131072
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 17.4587904[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 131072
X_prescans = 0
X_resolution = 57.27773672[mHz]
X_sweep = 7.50750751[kHz]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 10.5[us]
X_acq_time = 17.4587904[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 27
Relaxation_delay = 14[s]
Temp_get = 26[dC]
Unblank_time = 2[us]
CHO
CHO
S
S
S
CHO
97



JEOL

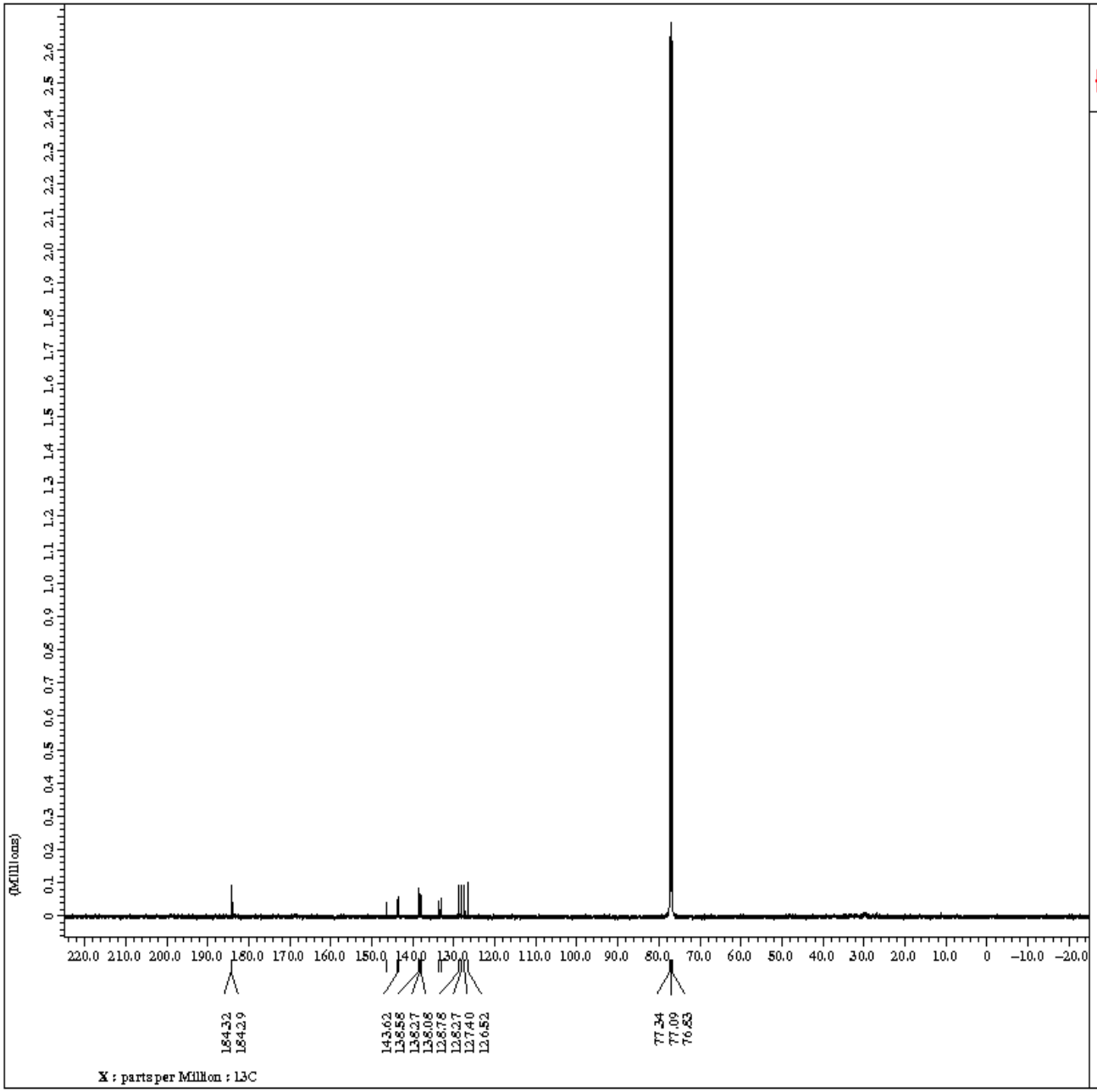
```
Filename          = ald-trimer-10.jdf
Author            = delta
Experiment        = single_pulse.exp
Sample_id         = S#656357
Solvent           = CHLOROFORM-D
Creation_time     = 15-OCT-2008 01:40:31
Revision_time     =  3-NOV-2008 11:49:17
Current_time      =  3-NOV-2008 11:53:19

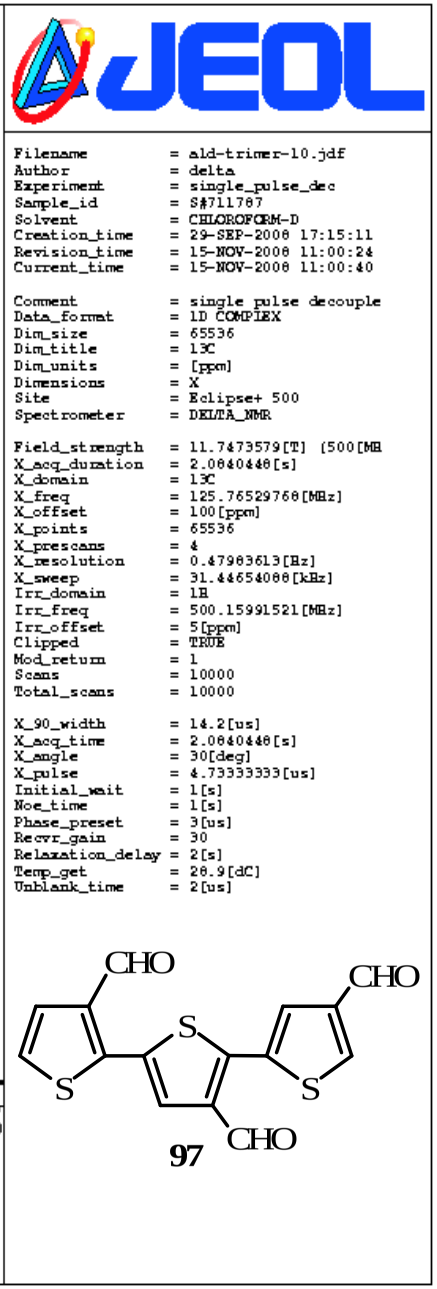
Comment           = Single Pulse Experime
Data_format       = 1D COMPLEX
Dim_size          = 131072
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

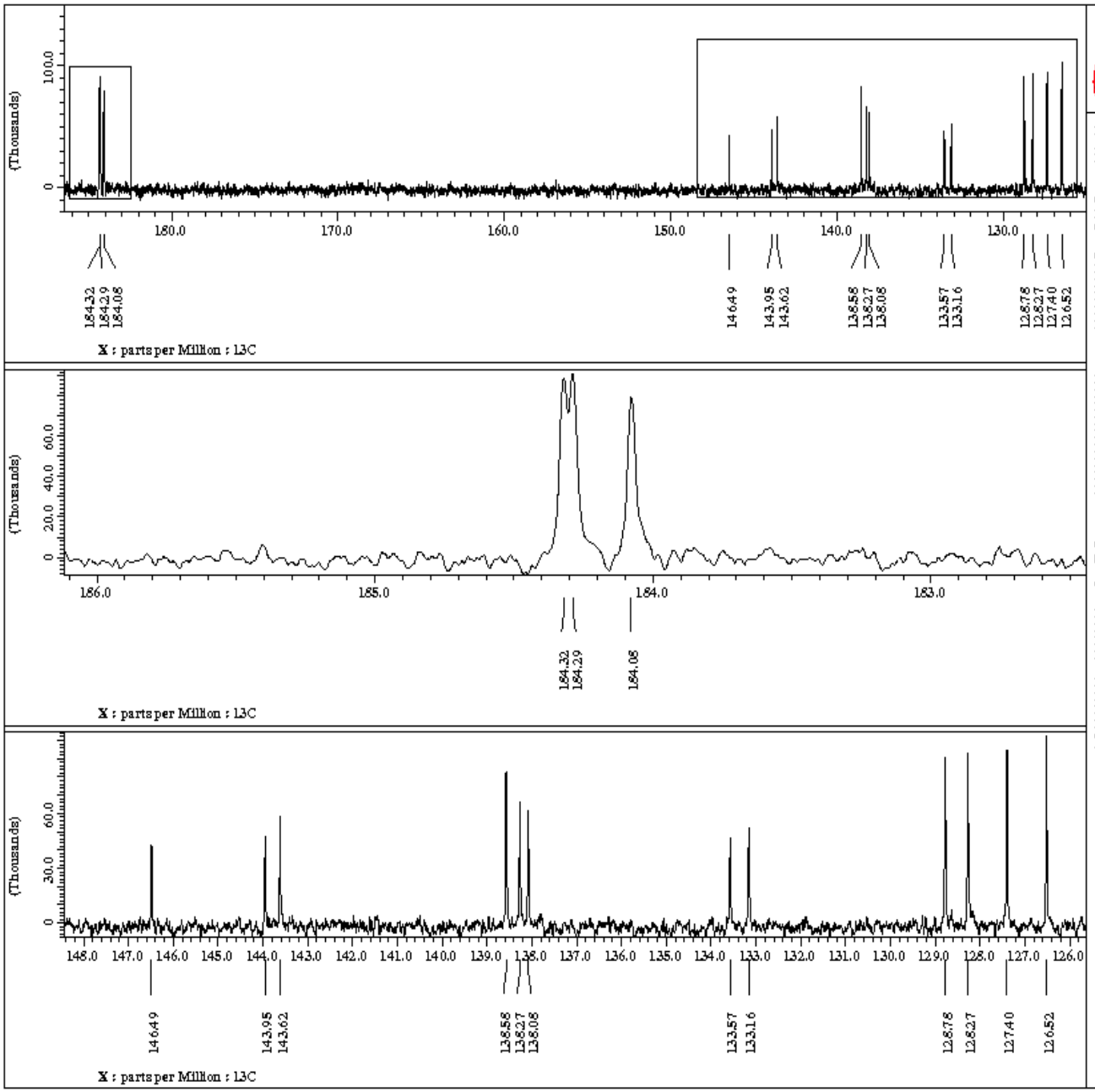
Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 17.4567904[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 5[ppm]
X_points          = 131072
X_prescans        = 0
X_resolution      = 57.27773672[mHz]
X_sweep           = 7.50750751[kHz]
Clipped           = FALSE
Mod_return        = 1
Scans             = 8
Total_scans       = 8

X_90_width        = 10.5[us]
X_acq_time        = 17.4567904[s]
X_angle           = 45[deg]
X_pulse           = 9.25[us]
Initial_wait      = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 27
Relaxation_delay  = 14[s]
Temp_get          = 26[dC]
Unblank_time      = 2[us]
```


97


(Millions)
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0 1.1 1.2 1.3 1.4 1.5 1.6 1.7 1.8 1.9 2.0 2.1 2.2 2.3 2.4 2.5 2.6
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
184.32
184.29
143.62
138.58
138.27
138.08
128.78
128.27
127.40
126.52
77.34
77.09
76.83
X : parts per Million : 13C


JEOL
Filename = ald-trimer-10.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = S#711787
Solvent = CHLOROFORM-D
Creation_time = 29-SEP-2008 17:15:11
Revision_time = 15-NOV-2008 11:00:24
Current_time = 15-NOV-2008 11:00:40
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 65536
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.0840448[s]
X_domain = 13C
X_freq = 125.76529760[MHz]
X_offset = 100[ppm]
X_points = 65536
X_prescans = 4
X_resolution = 0.47983613[Hz]
X_sweep = 31.44654088[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5[ppm]
Clipped = TRUE
Mod_return = 1
Scans = 10000
Total_scans = 10000
X_90_width = 14.2[us]
X_acq_time = 2.0840448[s]
X_angle = 30[deg]
X_pulse = 4.73333333[us]
Initial_wait = 1[s]
Noe_time = 1[s]
Phase_preset = 3[us]
Recvr_gain = 30
Relaxation_delay = 2[s]
Temp_get = 28.9[dC]
Unblank_time = 2[us]
CHO
CHO
S
S
S
CHO
97

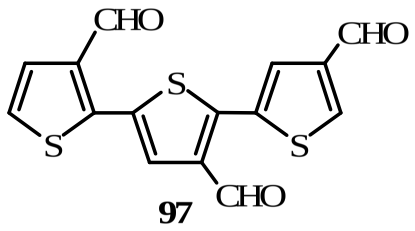



```
Filename          = ald-trimer-10.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#711707
Solvent           = CHLOROFORM-D
Creation_time     = 29-SEP-2008 17:15:11
Revision_time     = 15-NOV-2008 11:00:24
Current_time      = 15-NOV-2008 11:07:15

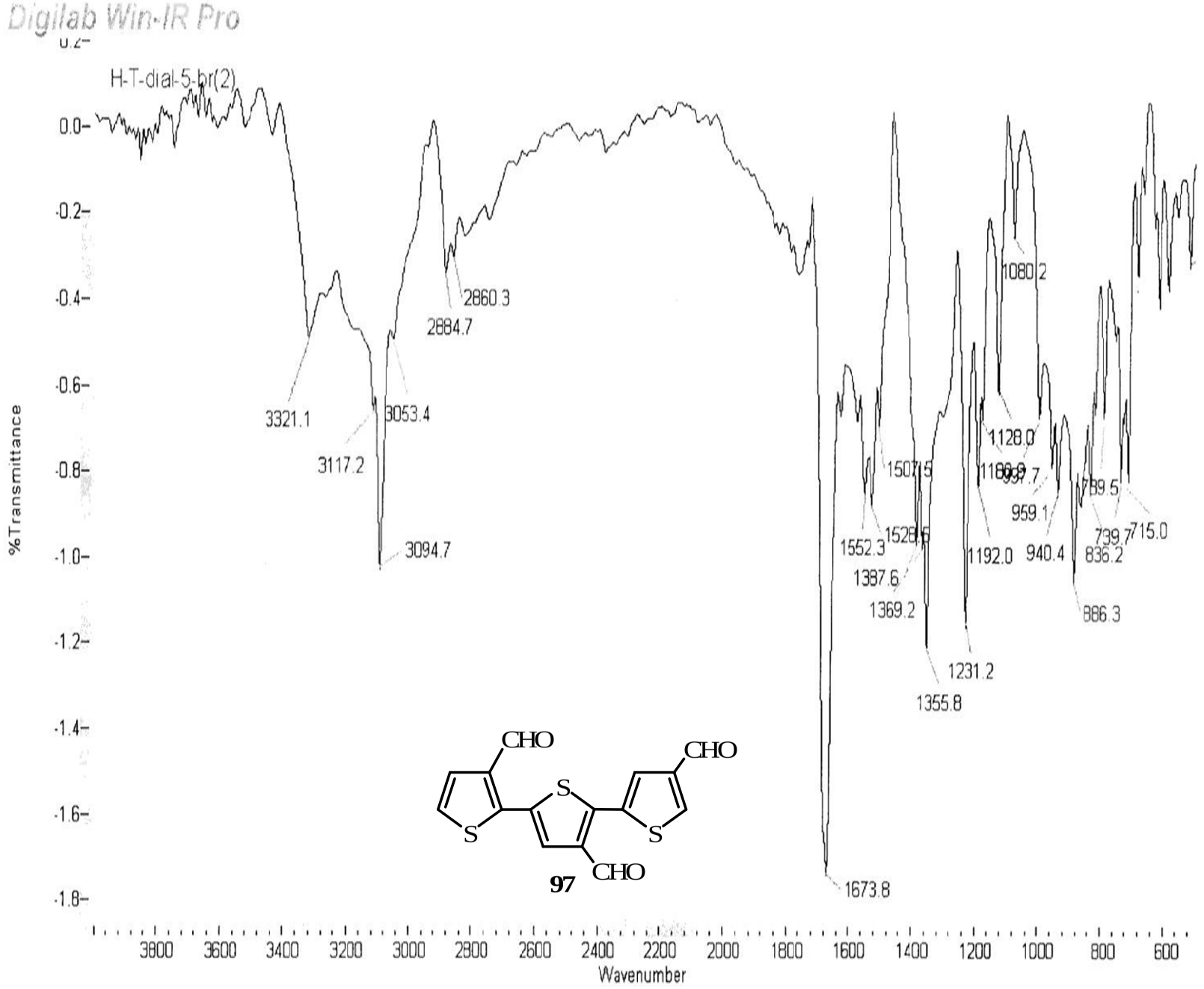
Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 65536
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 2.0840448[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 65536
X_prescans        = 4
X_resolution      = 0.47983613[Hz]
X_sweep           = 31.44654088[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5[ppm]
Clipped           = TRUE
Mod_return        = 1
Scans             = 10000
Total_scans       = 10000

X_90_width        = 14.2[us]
X_acq_time        = 2.0840448[s]
X_angle           = 30[deg]
X_pulse           = 4.73333333[us]
Initial_wait      = 1[s]
Noe_time          = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 30
Relaxation_delay  = 2[s]
Temp_get          = 28.9[dC]
Unblank_time      = 2[us]
```



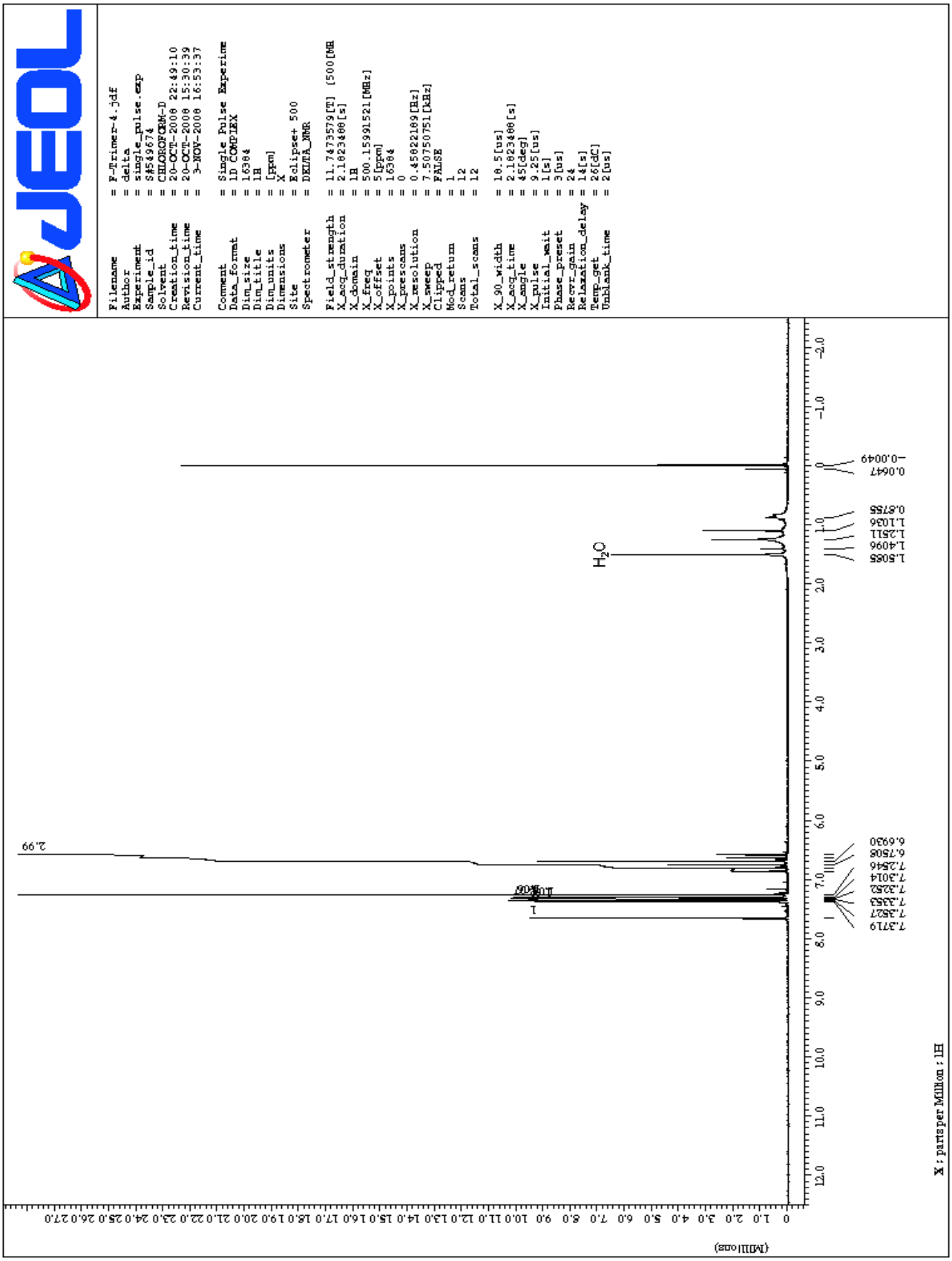
97

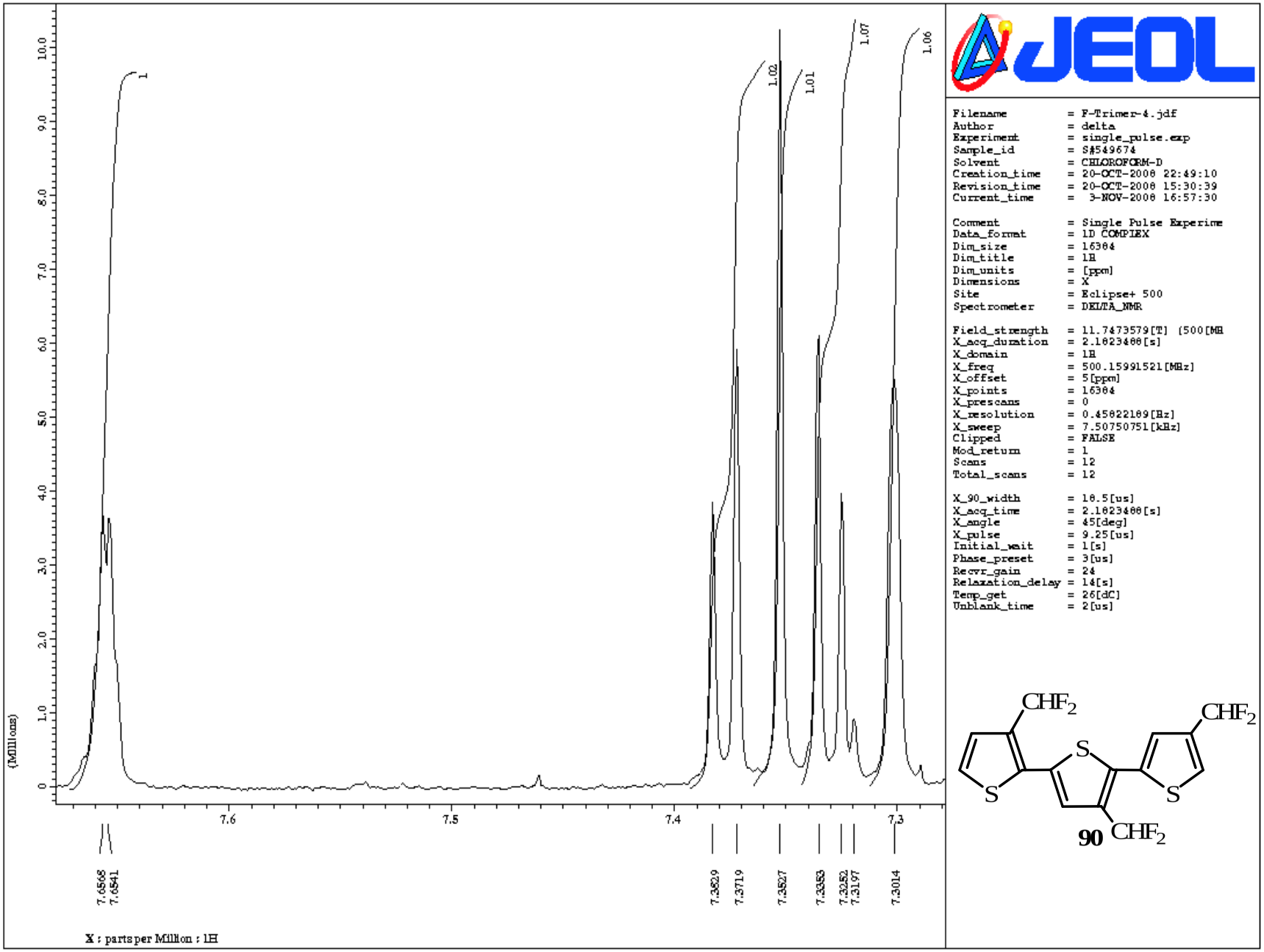

Digilab Win-IR Pro
H-T-dial-5-br(2)
%Transmittance
Wavenumber
3321.1
3117.2
3053.4
3094.7
2884.7
2860.3
1673.8
1552.3
1507.5
1387.6
1369.2
1355.8
1231.2
1192.0
1128.0
1080.2
959.1
940.4
886.3
836.2
739.7
715.0
CHO
CHO
CHO
S
S
S

97

APPENDIX 16

^{1}H, ^{19}F NMR and IR spectra of 3,4',4''-tris(difluoromethyl)-2,2':5',2''-terthiophene (**90**)


Filename = F-Trimer-4.jdf
Author = delta
Experiment = single_pulse.exp
Sample_id = SAS49674
Solvent = CHLOROFORM-D
Creation_time = 20-OCT-2008 22:49:10
Revision_time = 20-OCT-2008 15:30:39
Current_time = 3-NOV-2008 16:53:37
Comment = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Clipped = FALSE
Mod_return = 1
Scans = 12
Total_scans = 12
X_90_width = 18.5[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 24
Relaxation_delay = 14[s]
Temp_get = 26[dC]
Unblank_time = 2[us]
H2O
2.99
1
X : parts per Million : 1H



JEOL

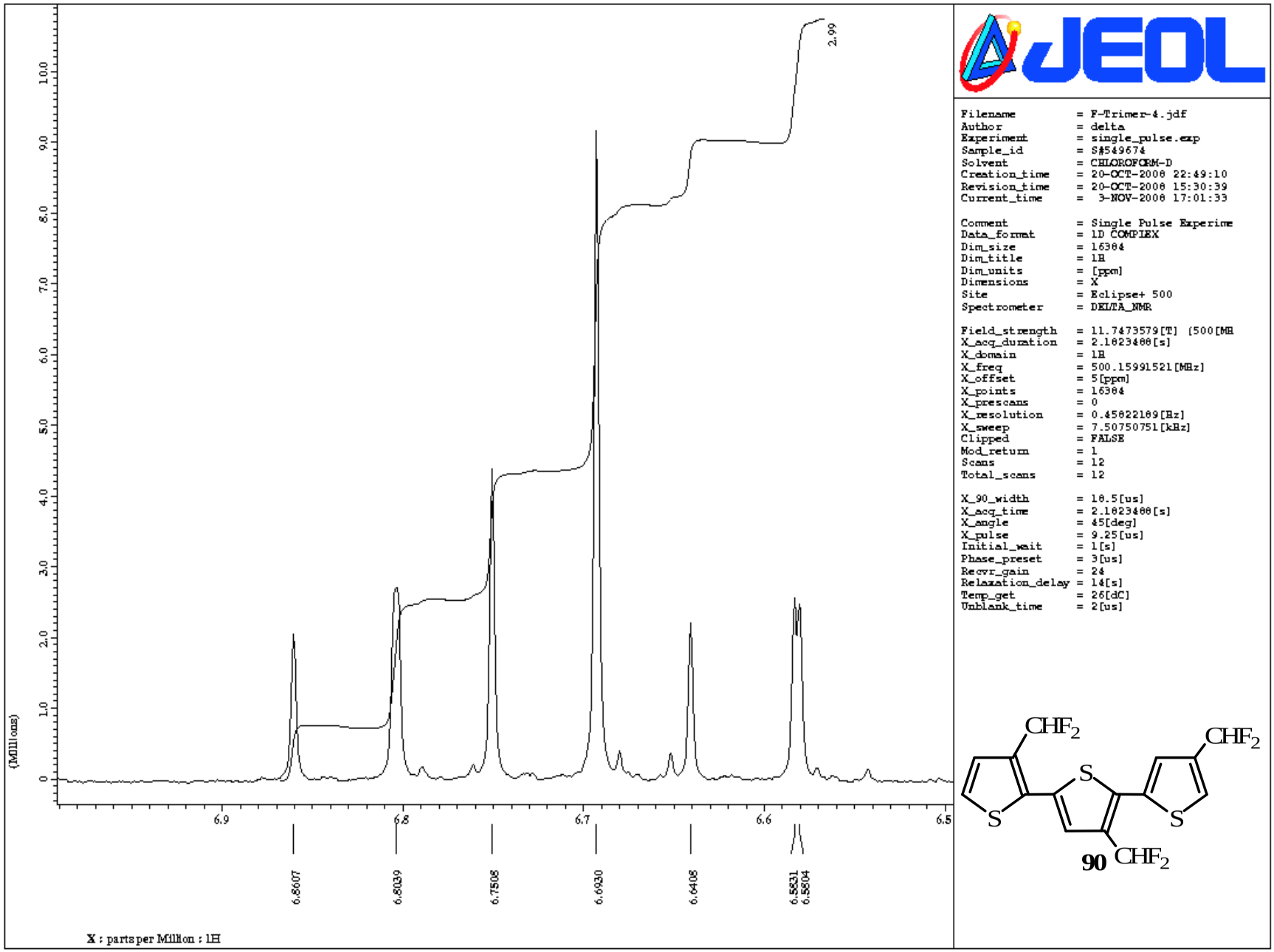
```
Filename          = F-Trimer-4.jdf
Author            = delta
Experiment        = single_pulse.exp
Sample_id         = S#549674
Solvent           = CHLOROFORM-D
Creation_time     = 20-OCT-2008 22:49:10
Revision_time     = 20-OCT-2008 15:30:39
Current_time      =  3-NOV-2008 16:57:30

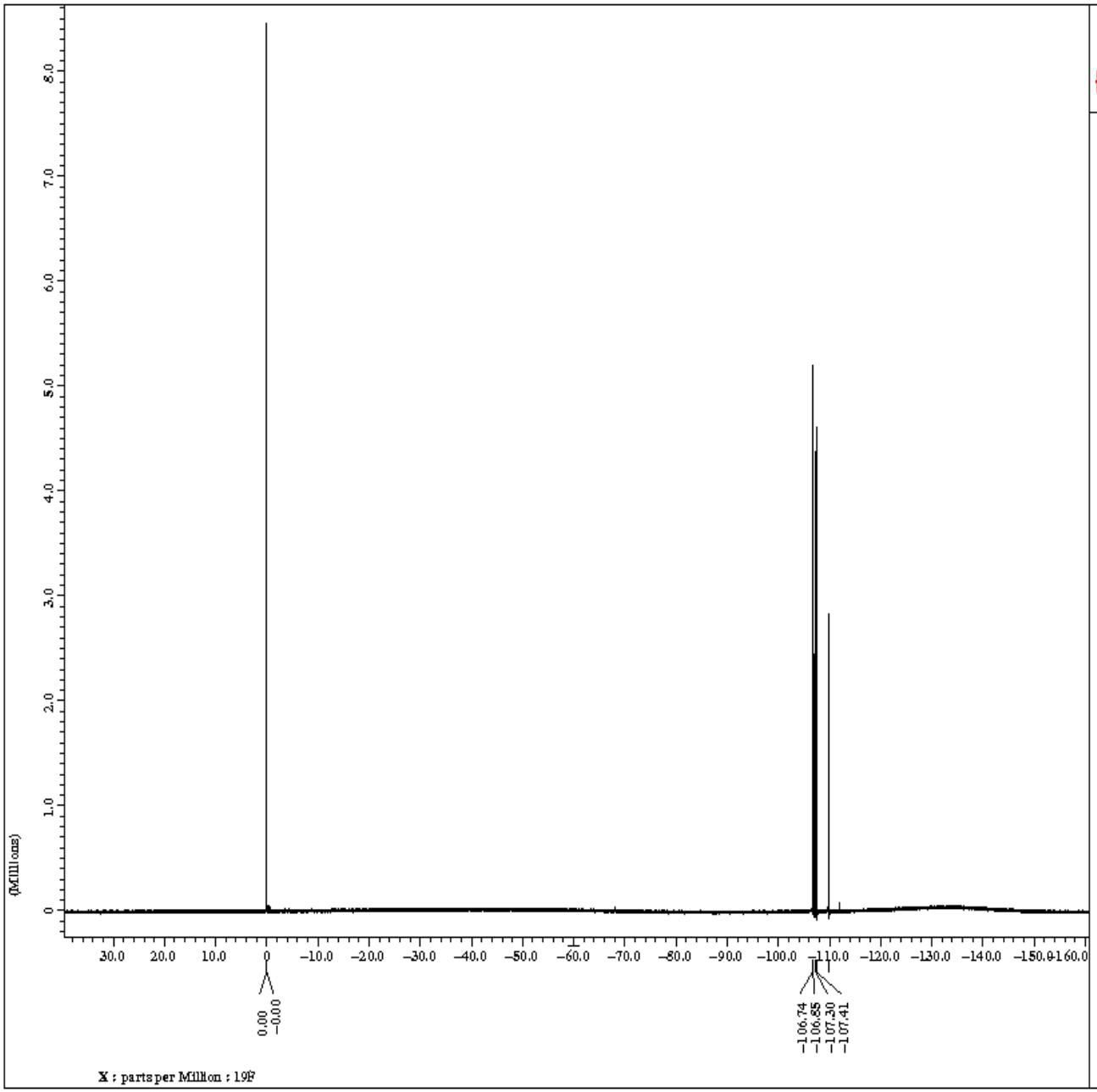
Comment           = Single Pulse Experime
Data_format       = 1D COMPLEX
Dim_size          = 16384
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

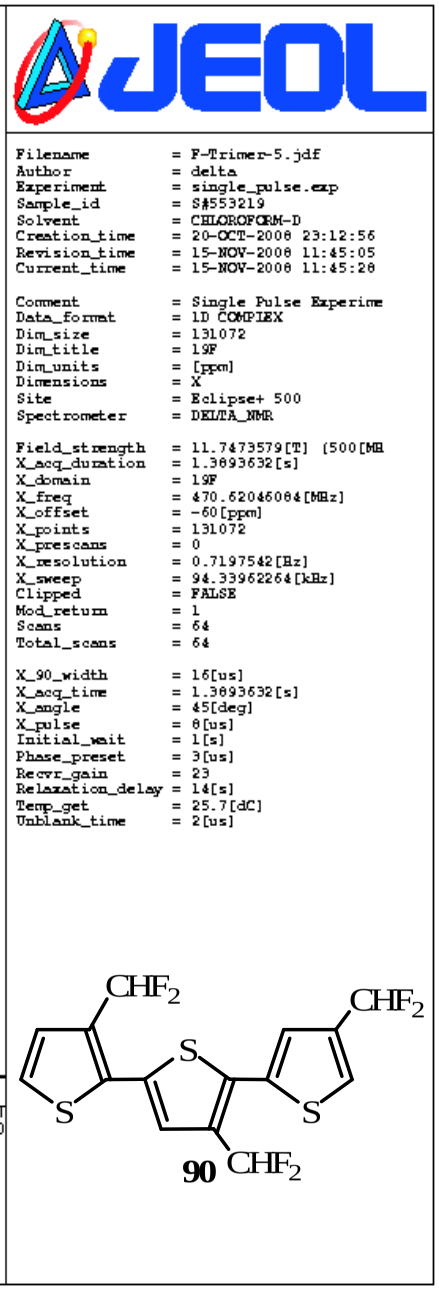
Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 2.1823488[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 5[ppm]
X_points          = 16384
X_prescans        = 0
X_resolution      = 0.45822189[Hz]
X_sweep           = 7.50750751[kHz]
Clipped           = FALSE
Mod_return        = 1
Scans             = 12
Total_scans       = 12

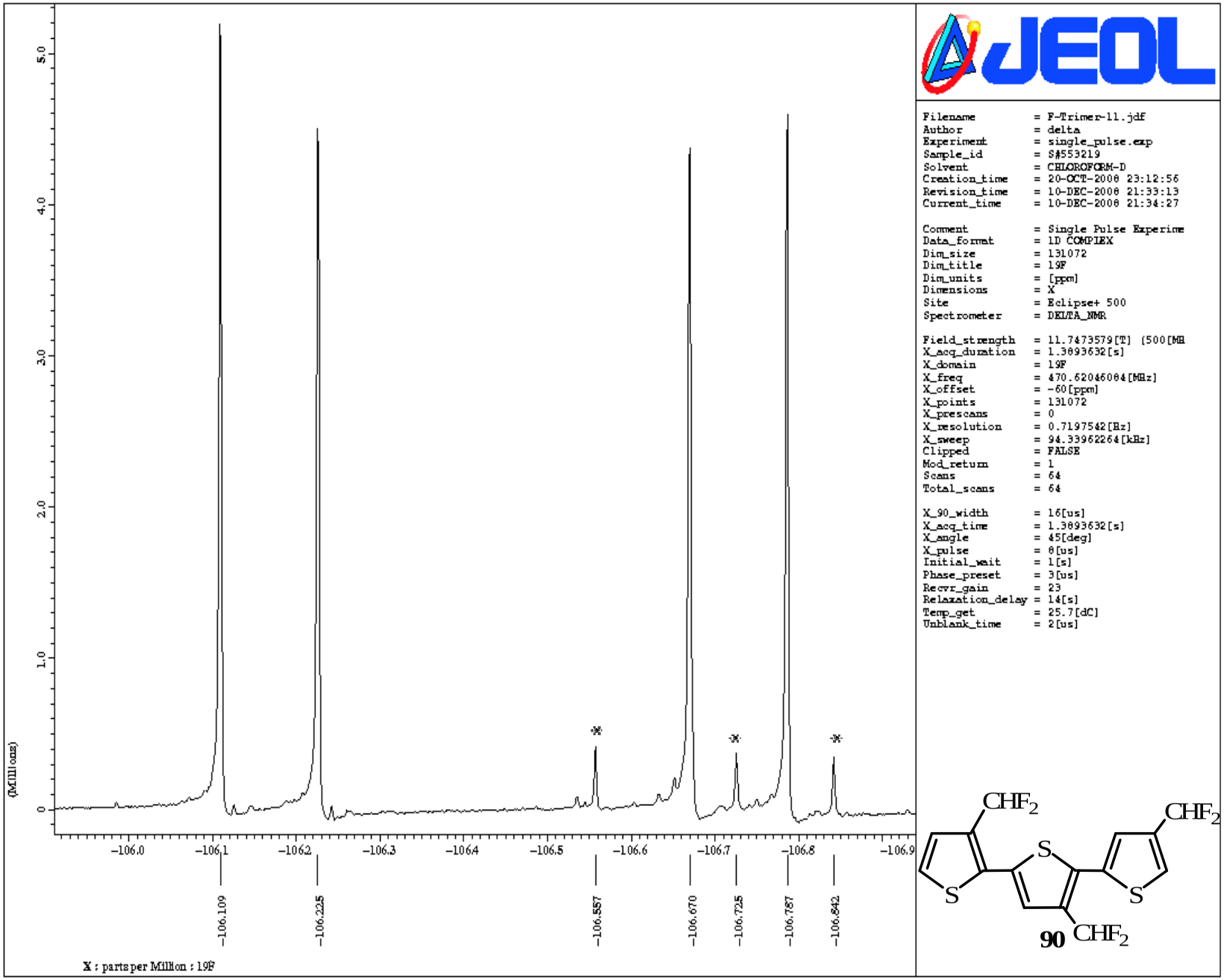
X_90_width        = 18.5[us]
X_acq_time        = 2.1823488[s]
X_angle           = 45[deg]
X_pulse           = 9.25[us]
Initial_wait      = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 24
Relaxation_delay  = 14[s]
Temp_get          = 26[dC]
Unblank_time      = 2[us]
```

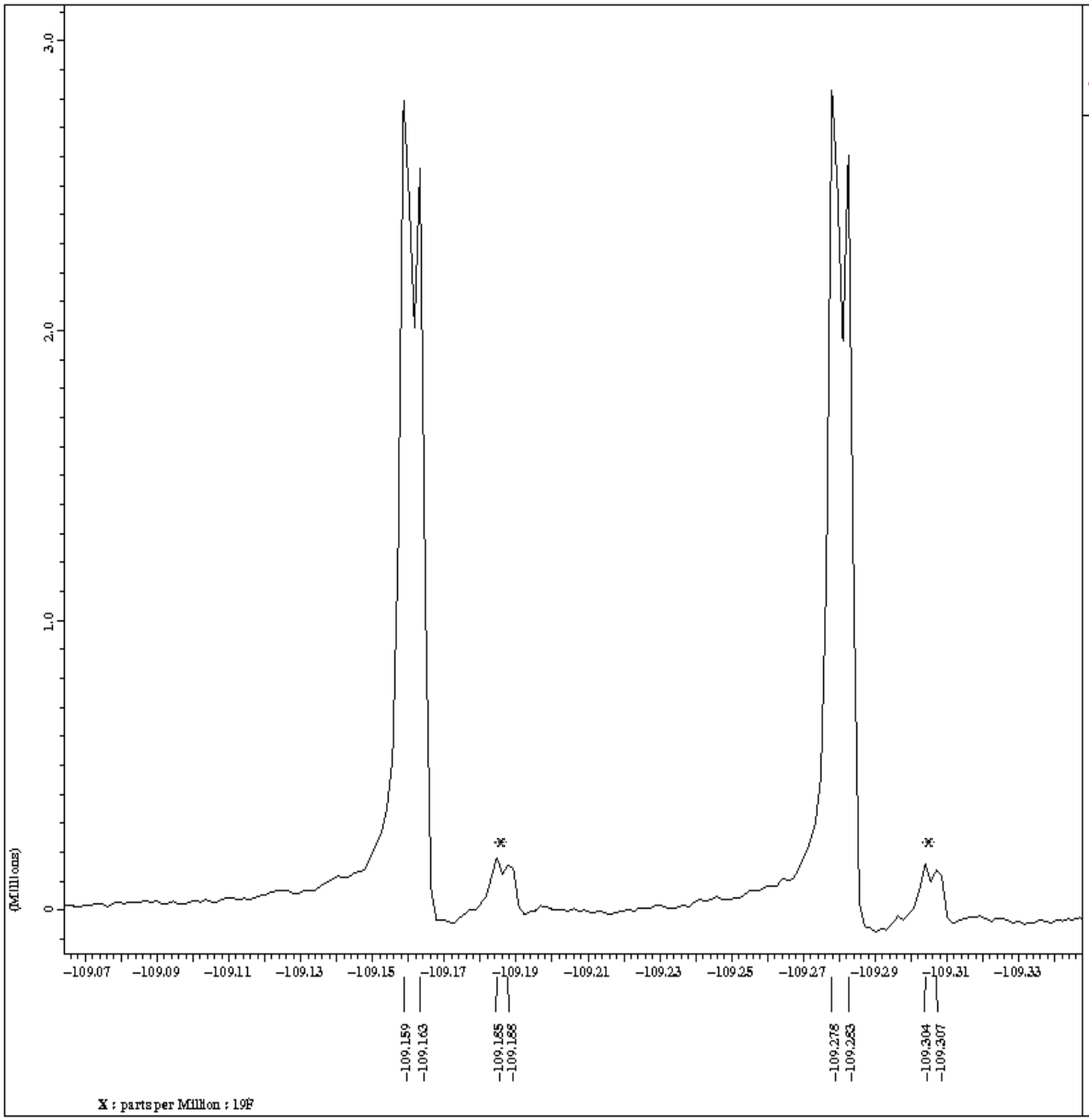

90


2.99
(Millions)
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
6.9
6.8
6.7
6.6
6.5
6.8607
6.8039
6.7508
6.6930
6.6408
6.5831
6.5804
X : parts per Million : 1H
Filename = F-Trimer-4.jdf
Author = delta
Experiment = single_pulse.exp
Sample_id = S#549674
Solvent = CHLOROFORM-D
Creation_time = 20-OCT-2008 22:49:10
Revision_time = 20-OCT-2008 15:30:39
Current_time = 3-NOV-2008 17:01:33
Comment = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Clipped = FALSE
Mod_return = 1
Scans = 12
Total_scans = 12
X_90_width = 10.5[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 24
Relaxation_delay = 14[s]
Temp_get = 26[dC]
Unblank_time = 2[us]
CHF2
CHF2
S
S
S
CHF2
90


(Millions)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
30.0 20.0 10.0 0 −10.0 −20.0 −30.0 −40.0 −50.0 −60.0 −70.0 −80.0 −90.0 −100.0 −110.0 −120.0 −130.0 −140.0 −150.0 −160.0
0.00
−0.00
−106.74
−106.85
−107.30
−107.41
X : parts per Million : 19F


JEOL
Filename = F-Trimer-5.jdf
Author = delta
Experiment = single_pulse.exp
Sample_id = S#553219
Solvent = CHLOROFORM-D
Creation_time = 20-OCT-2008 23:12:56
Revision_time = 15-NOV-2008 11:45:05
Current_time = 15-NOV-2008 11:45:20
Comment = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 131072
Dim_title = 19F
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 1.3893632[s]
X_domain = 19F
X_freq = 470.62046084[MHz]
X_offset = -60[ppm]
X_points = 131072
X_prescans = 0
X_resolution = 0.7197542[Hz]
X_sweep = 94.33962264[kHz]
Clipped = FALSE
Mod_return = 1
Scans = 64
Total_scans = 64
X_90_width = 16[us]
X_acq_time = 1.3893632[s]
X_angle = 45[deg]
X_pulse = 8[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 23
Relaxation_delay = 14[s]
Temp_get = 25.7[dC]
Unblank_time = 2[us]
CHF2
CHF2
S
S
S
CHF2
90


(Millions)
5.0
4.0
3.0
2.0
1.0
0
-106.0
-106.1
-106.2
-106.3
-106.4
-106.5
-106.6
-106.7
-106.8
-106.9
-106.109
-106.225
-106.557
-106.670
-106.725
-106.787
-106.842
X : parts per Million : 19F
Filename = F-Trimer-11.jdf
Author = delta
Experiment = single_pulse.exp
Sample_id = S#553219
Solvent = CHLOROFORM-D
Creation_time = 20-OCT-2008 23:12:56
Revision_time = 10-DEC-2008 21:33:13
Current_time = 10-DEC-2008 21:34:27
Comment = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 131072
Dim_title = 19F
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 1.3893632[s]
X_domain = 19F
X_freq = 470.62046064[MHz]
X_offset = -60[ppm]
X_points = 131072
X_prescans = 0
X_resolution = 0.7197542[Hz]
X_sweep = 94.33962264[kHz]
Clipped = FALSE
Mod_return = 1
Scans = 64
Total_scans = 64
X_90_width = 16[us]
X_acq_time = 1.3893632[s]
X_angle = 45[deg]
X_pulse = 8[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 23
Relaxation_delay = 14[s]
Temp_get = 25.7[dC]
Unblank_time = 2[us]
CHF2
CHF2
S
S
S
CHF2
90



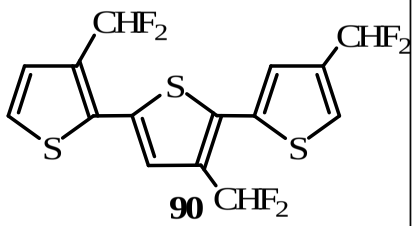
JEOL

```
Filename          = F-Trimer-11.jdf
Author            = delta
Experiment        = single_pulse.exp
Sample_id         = S#553219
Solvent           = CHLOROFORM-D
Creation_time     = 20-OCT-2008 23:12:56
Revision_time     = 10-DEC-2008 21:40:10
Current_time      = 10-DEC-2008 21:40:35

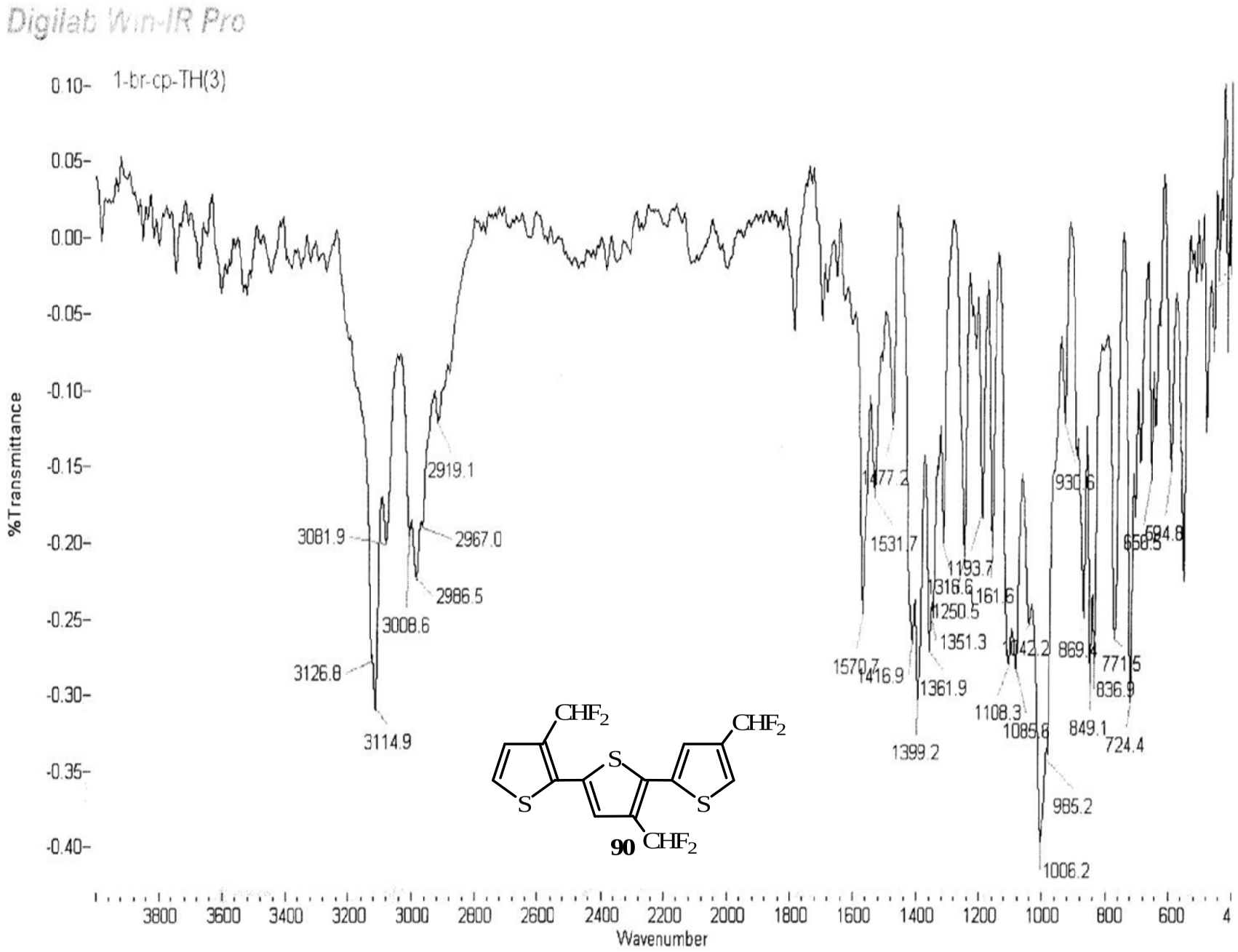
Comment           = Single Pulse Experime
Data_format       = 1D COMPLEX
Dim_size          = 131072
Dim_title         = 19F
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

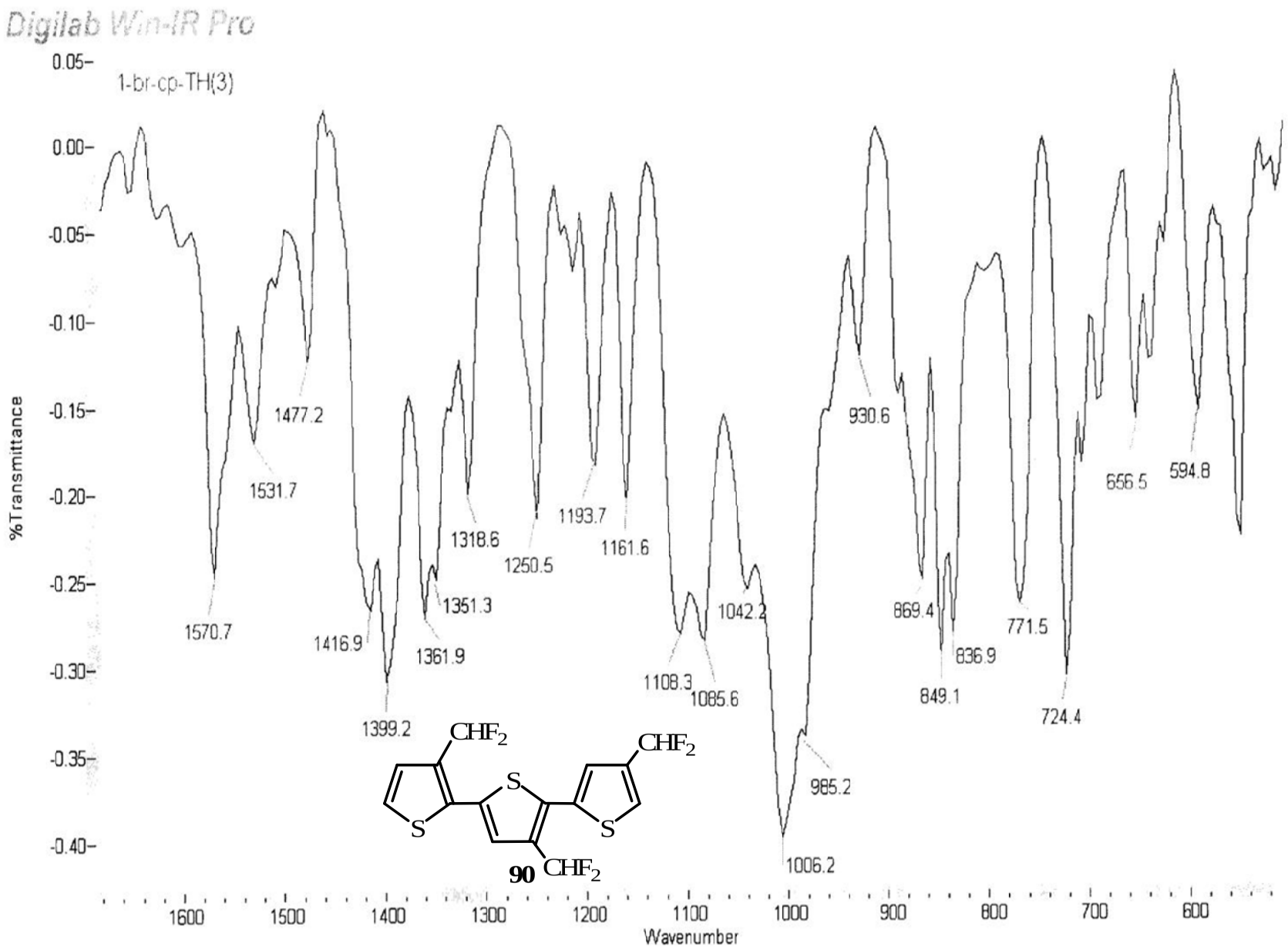
Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 1.3093632[s]
X_domain          = 19F
X_freq            = 470.62046084[MHz]
X_offset          = -60[ppm]
X_points          = 131072
X_prescans        = 0
X_resolution      = 0.7197542[Hz]
X_sweep           = 94.33962264[kHz]
Clipped           = FALSE
Mod_return        = 1
Scans             = 64
Total_scans       = 64

X_90_width        = 16[us]
X_acq_time        = 1.3093632[s]
X_angle           = 45[deg]
X_pulse           = 8[us]
Initial_wait      = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 23
Relaxation_delay  = 14[s]
Temp_get          = 25.7[dC]
Unblank_time      = 2[us]
```



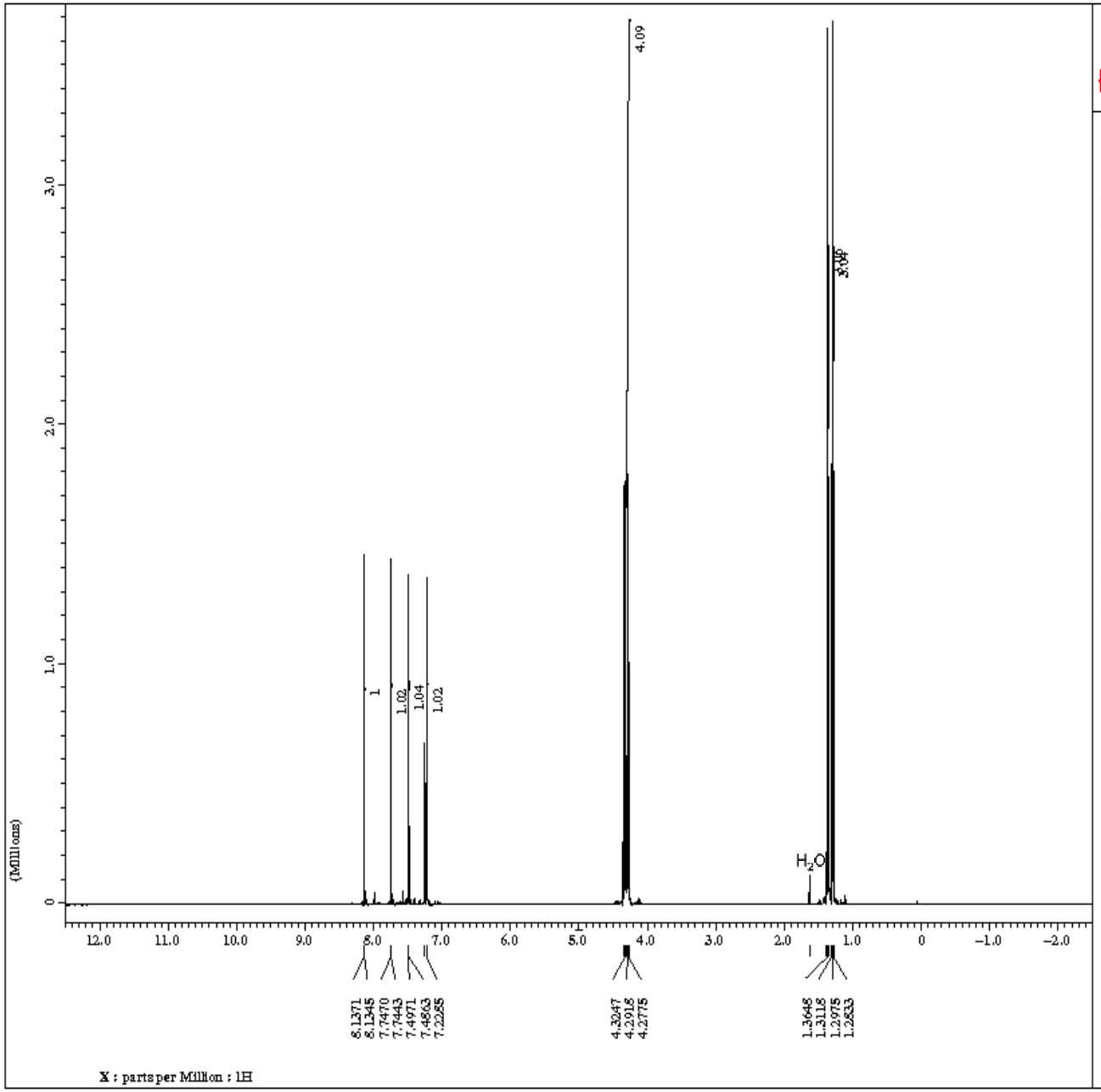
90


Digilab Win-IR Pro
1-br-cp-TH(3)
%Transmittance
Wavenumber
3081.9
2967.0
2919.1
2986.5
3008.6
3126.8
3114.9
1570.7
1477.2
1531.7
1416.9
1399.2
1361.9
1351.3
1316.6
1250.5
1193.7
1161.6
1108.3
1085.6
1006.2
985.2
930.6
869.4
849.1
836.9
771.5
724.4
656.5
584.8
CHF2
S
90


Digilab Win-IR Pro
1-br-cp-TH(3)
%Transmittance
Wavenumber
0.05
0.00
-0.05
-0.10
-0.15
-0.20
-0.25
-0.30
-0.35
-0.40
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
1570.7
1531.7
1477.2
1416.9
1399.2
1361.9
1351.3
1318.6
1250.5
1193.7
1161.6
1108.3
1085.6
1042.2
1006.2
985.2
930.6
869.4
849.1
836.9
771.5
724.4
666.5
594.8
CHF2
CHF2
CHF2
S
S
S
90

APPENDIX 17

^{1}H, ^{13}C NMR and IR spectra of diethyl 2,2'-bithiophene-3,4-dicarboxylate (**104**)

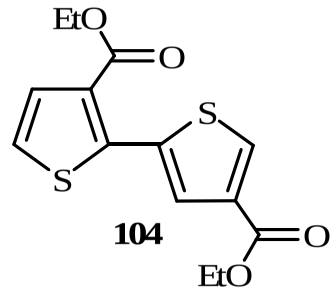


Filename = H-T-Et-Th-Car-4.jdf
Author = delta
Experiment = single_pulse.exp
Sample_id = S#654219
Solvent = CHLOROFORM-D
Creation_time = 17-JUL-2008 01:15:23
Revision_time = 6-NOV-2008 19:08:32
Current_time = 6-NOV-2008 19:08:55

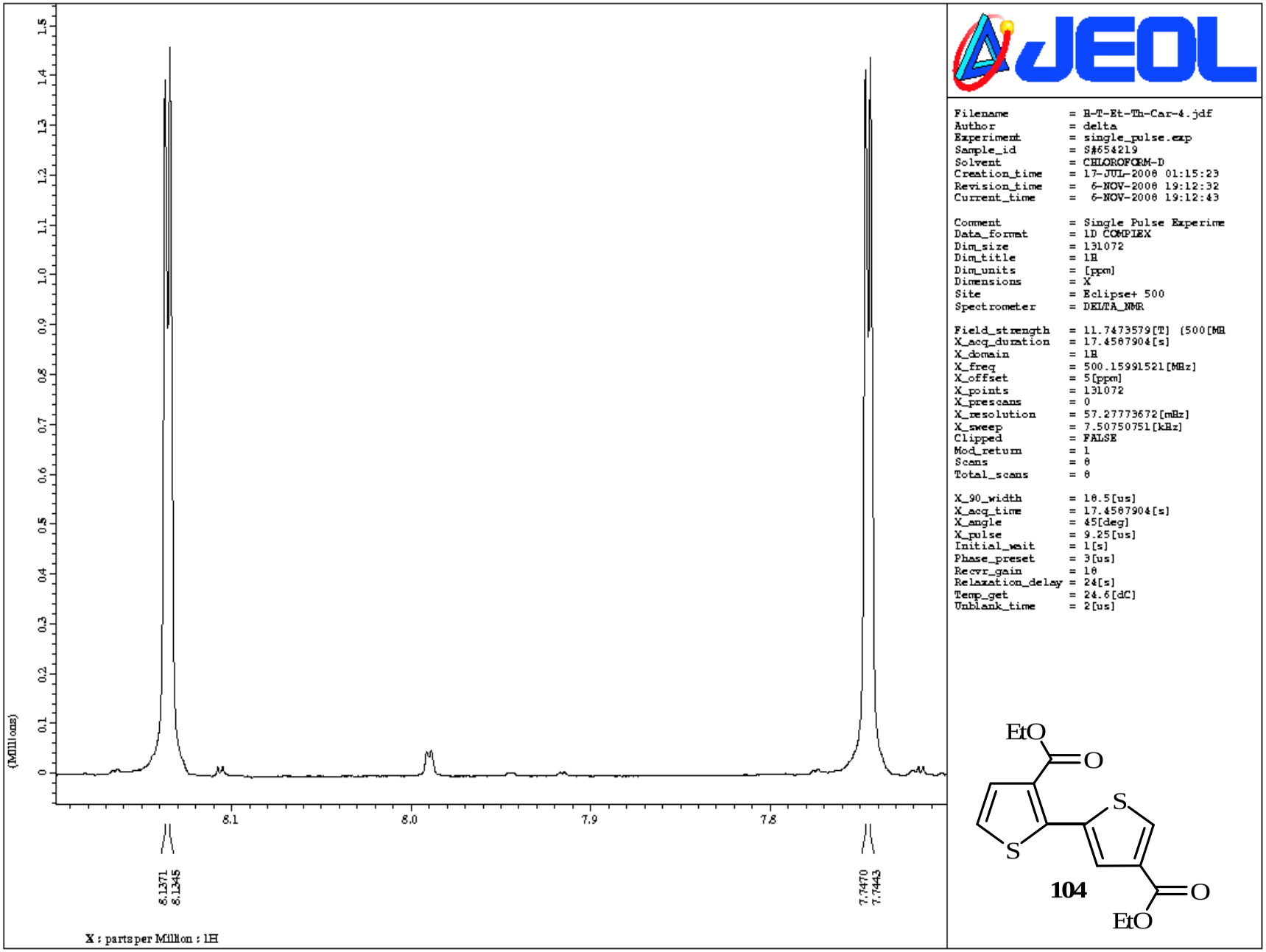
Comment = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 131072
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR

Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 17.4587904[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 131072
X_prescans = 0
X_resolution = 57.27773672[mHz]
X_sweep = 7.50750751[kHz]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8

X_90_width = 10.5[us]
X_acq_time = 17.4587904[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 18
Relaxation_delay = 24[s]
Temp_get = 24.6[dC]
Unblank_time = 2[us]



104



JEOL

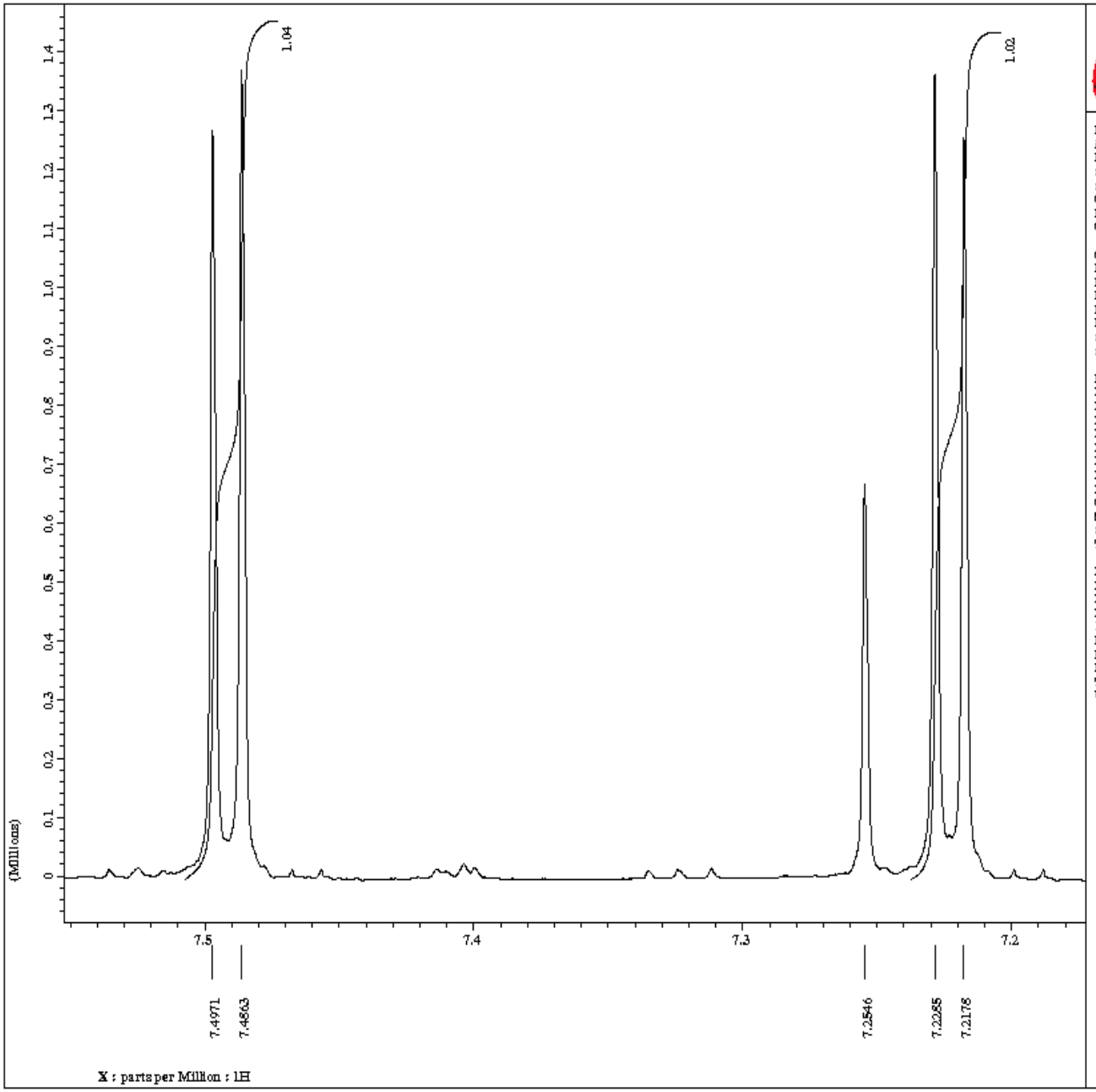
```
Filename          = H-T-Et-Th-Car-4.jdf
Author            = delta
Experiment        = single_pulse.exp
Sample_id         = S#654219
Solvent           = CHLOROFORM-D
Creation_time     = 17-JUL-2008 01:15:23
Revision_time     =  6-NOV-2008 19:12:32
Current_time      =  6-NOV-2008 19:12:43

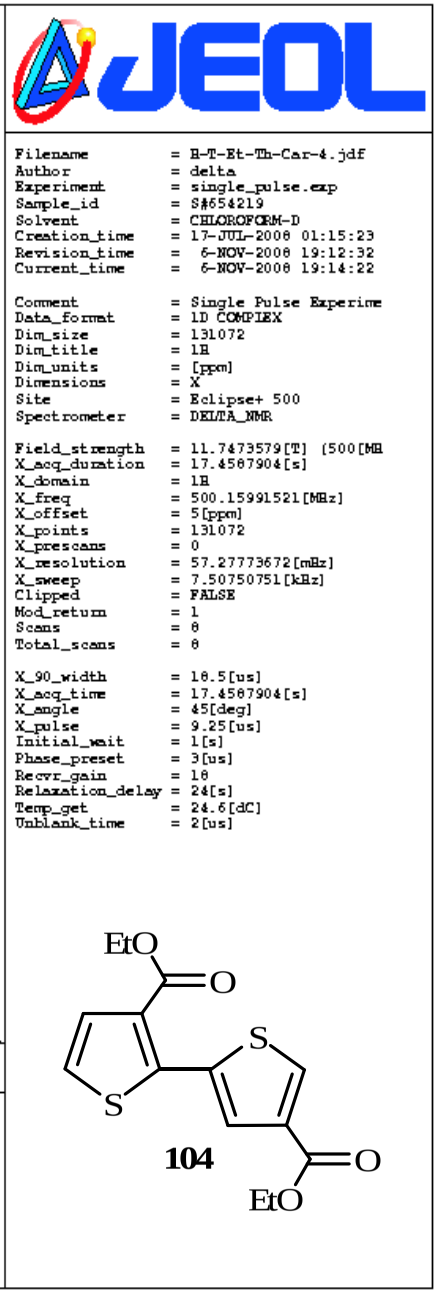
Comment           = Single Pulse Experime
Data_format       = 1D COMPLEX
Dim_size          = 131072
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

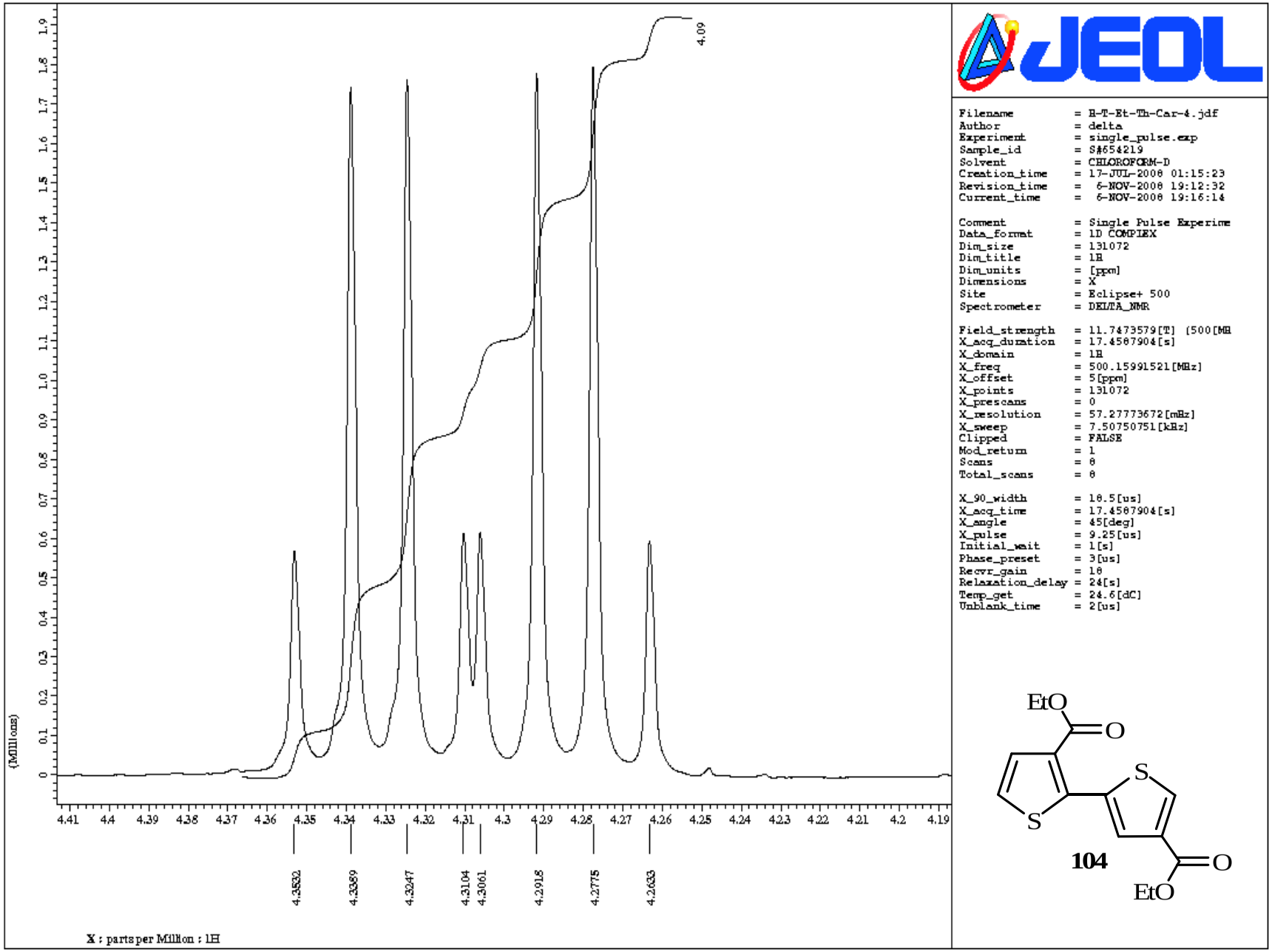
Field_strength    = 11.7473579[T]  (500[MH
X_acq_duration    = 17.4567904[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 5[ppm]
X_points          = 131072
X_prescans        = 0
X_resolution      = 57.27773672[mHz]
X_sweep           = 7.50750751[kHz]
Clipped           = FALSE
Mod_return        = 1
Scans             = 8
Total_scans       = 8

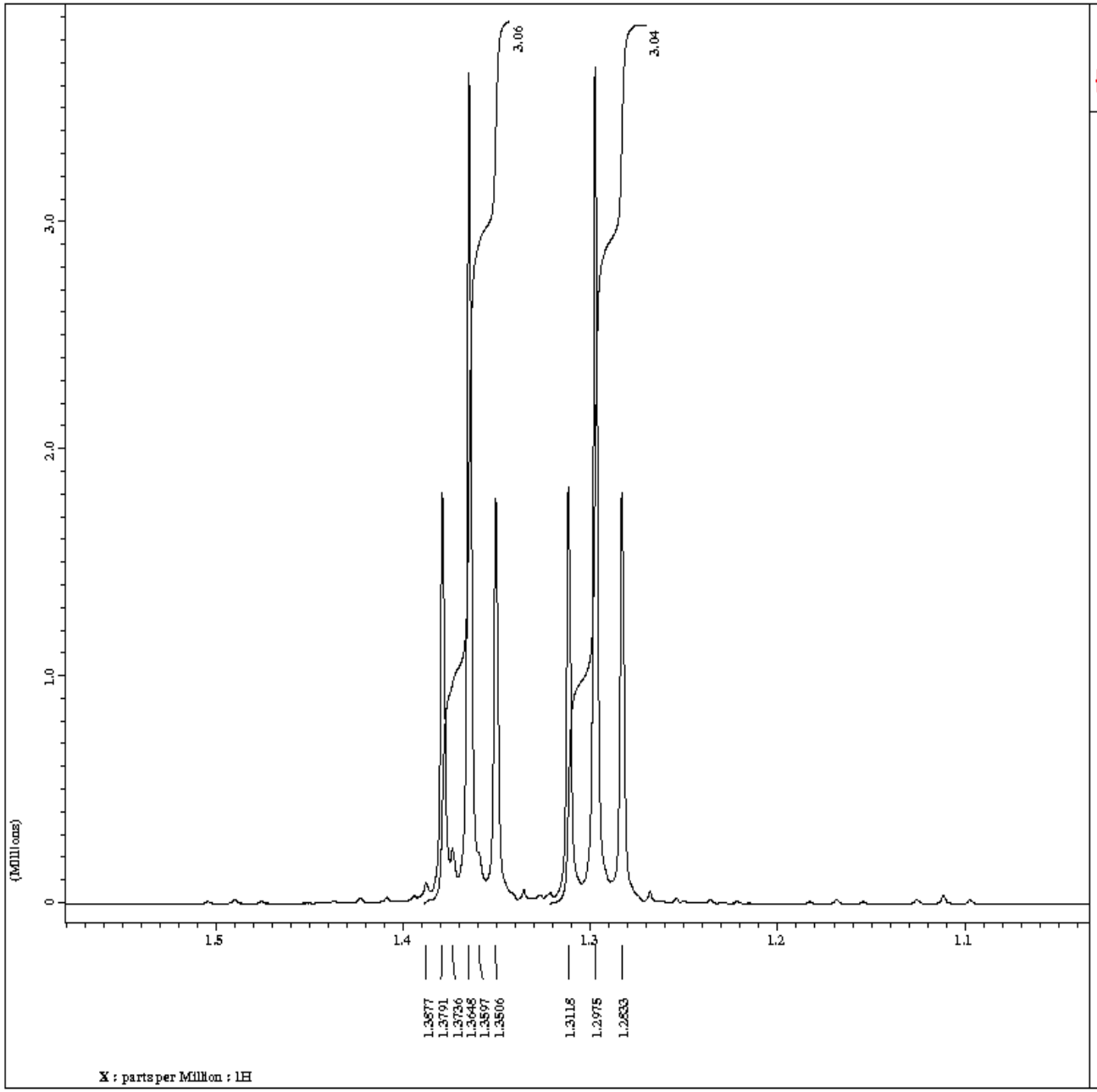
X_90_width        = 10.5[us]
X_acq_time        = 17.4567904[s]
X_angle           = 45[deg]
X_pulse           = 9.25[us]
Initial_wait      = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 10
Relaxation_delay  = 24[s]
Temp_get          = 24.6[dC]
Unblank_time      = 2[us]
```


104


1.04
1.02
(Millions)
7.5
7.4
7.3
7.2
7.4971
7.4563
7.2546
7.2285
7.2178
X : parts per Million : 1H


JEOL
Filename = H-T-Et-Th-Car-4.jdf
Author = delta
Experiment = single_pulse.exp
Sample_id = S#654219
Solvent = CHLOROFORM-D
Creation_time = 17-JUL-2008 01:15:23
Revision_time = 6-NOV-2008 19:12:32
Current_time = 6-NOV-2008 19:14:22
Comment = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 131072
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 17.4587904[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 131072
X_prescans = 0
X_resolution = 57.27773672[mHz]
X_sweep = 7.50750751[kHz]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 10.5[us]
X_acq_time = 17.4587904[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 10
Relaxation_delay = 24[s]
Temp_get = 24.6[dC]
Unblank_time = 2[us]
EtO
O
S
S
O
EtO
104


4.09
(Millions)
4.41 4.4 4.39 4.38 4.37 4.36 4.35 4.34 4.33 4.32 4.31 4.3 4.29 4.28 4.27 4.26 4.25 4.24 4.23 4.22 4.21 4.2 4.19
4.3532
4.3369
4.3247
4.3104
4.3061
4.2918
4.2775
4.2633
X : parts per Million : 1H
JEOL
Filename = H-T-Et-Th-Car-4.jdf
Author = delta
Experiment = single_pulse.exp
Sample_id = S#65&219
Solvent = CHLOROFORM-D
Creation_time = 17-JUL-2008 01:15:23
Revision_time = 6-NOV-2008 19:12:32
Current_time = 6-NOV-2008 19:16:14
Comment = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 131072
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 17.4587904[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 131072
X_prescans = 0
X_resolution = 57.27773672[mHz]
X_sweep = 7.50750751[kHz]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 18.5[us]
X_acq_time = 17.4587904[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 18
Relaxation_delay = 24[s]
Temp_get = 24.6[dC]
Unblank_time = 2[us]
EtO
O
S
S
O
EtO
104



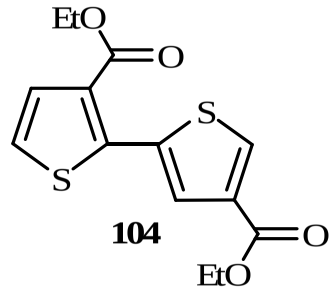
JEOL

```
Filename          = H-T-Et-Th-Car-4.jdf
Author            = delta
Experiment        = single_pulse.exp
Sample_id         = S#654219
Solvent           = CHLOROFORM-D
Creation_time     = 17-JUL-2008 01:15:23
Revision_time     =  6-NOV-2008 19:12:32
Current_time      =  6-NOV-2008 19:16:05

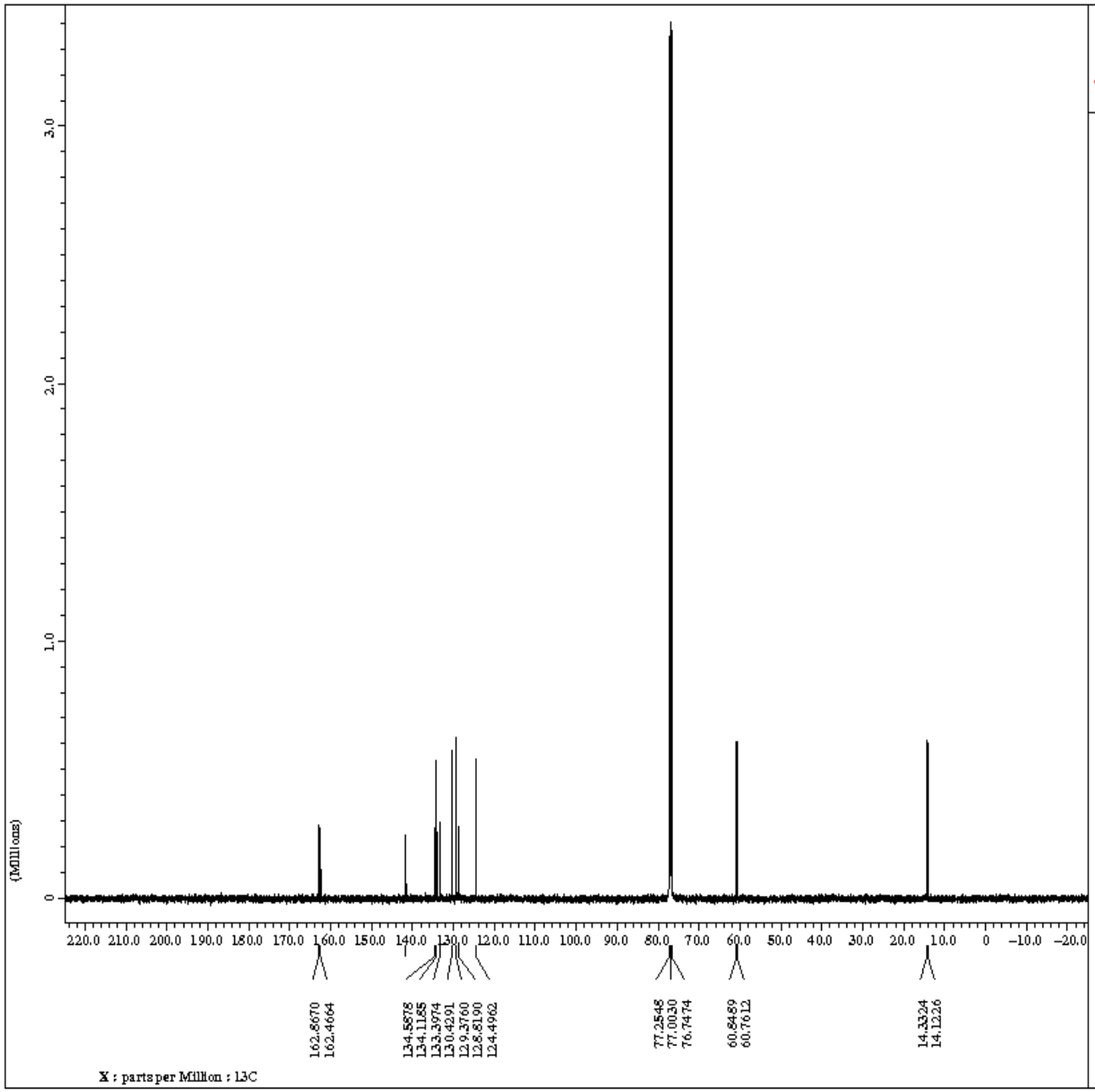
Comment           = Single Pulse Experime
Data_format       = 1D COMPLEX
Dim_size          = 131072
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 17.4587904[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 5[ppm]
X_points          = 131072
X_prescans        = 0
X_resolution      = 57.27773672[mHz]
X_sweep           = 7.50750751[kHz]
Clipped           = FALSE
Mod_return        = 1
Scans             = 8
Total_scans       = 8

X_90_width        = 10.5[us]
X_acq_time        = 17.4587904[s]
X_angle           = 45[deg]
X_pulse           = 9.25[us]
Initial_wait      = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 10
Relaxation_delay  = 24[s]
Temp_get          = 24.6[dC]
Unblank_time      = 2[us]
```



104

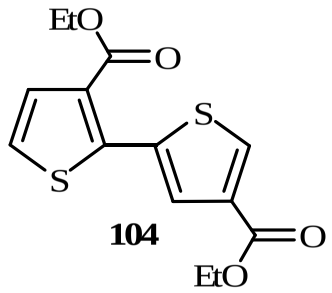


Filename = H-T-Et-Th-Car-3.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = S#662792
Solvent = CHLOROFORM-D
Creation_time = 17-JUL-2008 03:20:05
Revision_time = 16-JUL-2008 20:45:34
Current_time = 2-NOV-2008 21:54:53

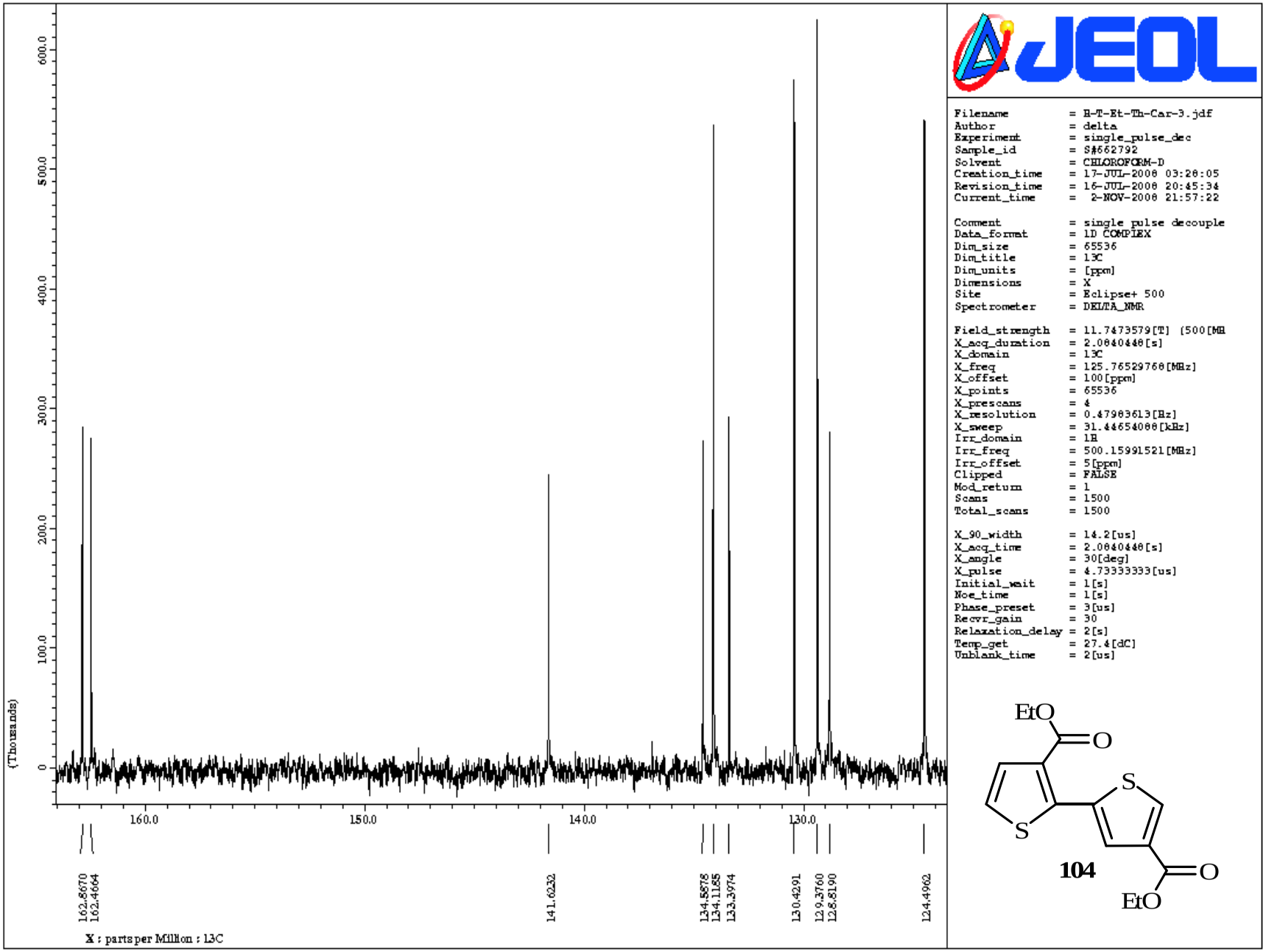
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 65536
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR

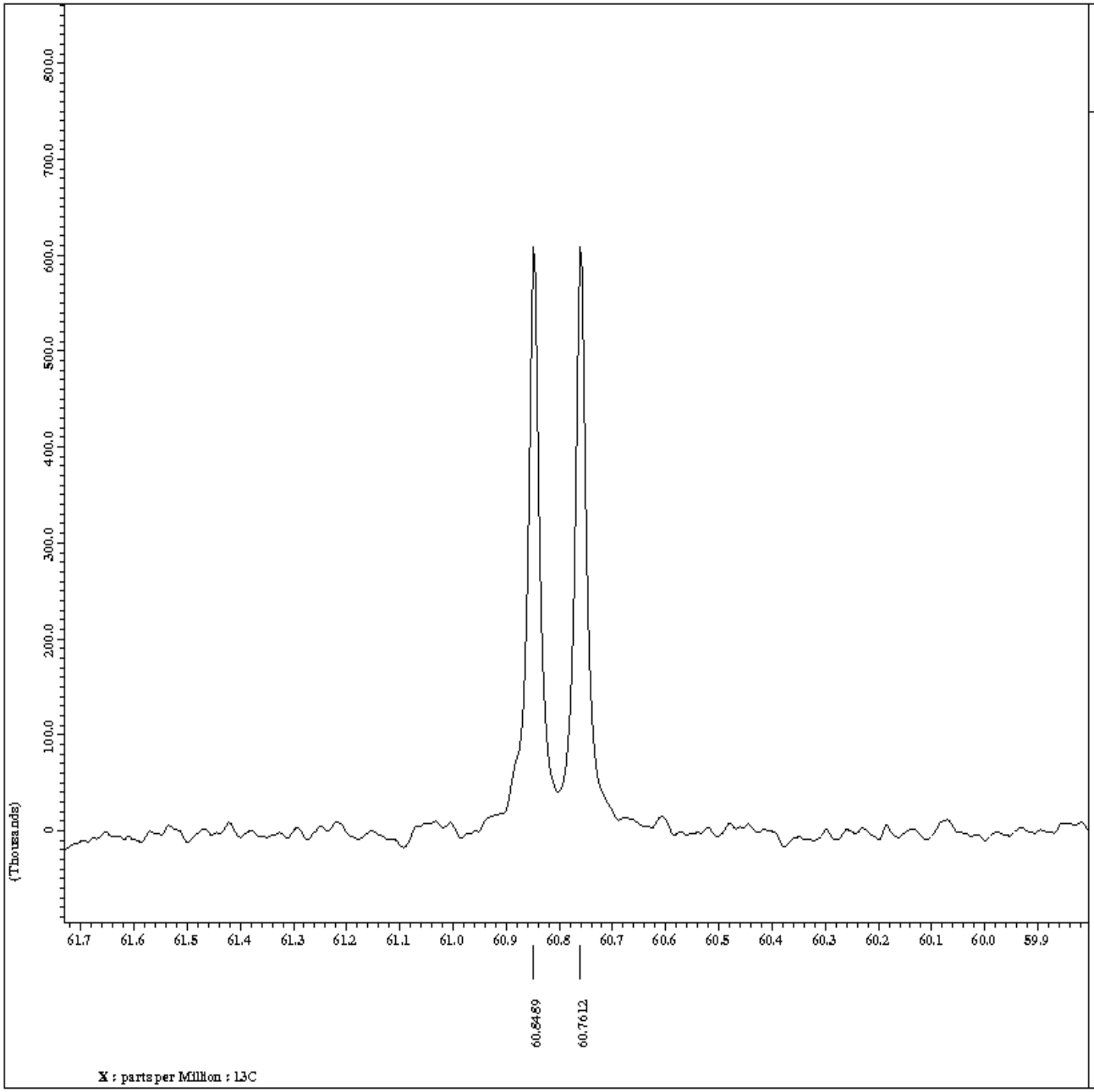
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.0840448[s]
X_domain = 13C
X_freq = 125.76529768[MHz]
X_offset = 100[ppm]
X_points = 65536
X_prescans = 4
X_resolution = 0.47983613[Hz]
X_sweep = 31.44654088[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 1500
Total_scans = 1500

X_90_width = 14.2[us]
X_acq_time = 2.0840448[s]
X_angle = 30[deg]
X_pulse = 4.73333333[us]
Initial_wait = 1[s]
Noe_time = 1[s]
Phase_preset = 3[us]
Recvr_gain = 30
Relaxation_delay = 2[s]
Temp_get = 27.4[dC]
Unblank_time = 2[us]



104


(Thousands)
600.0
500.0
400.0
300.0
200.0
100.0
0
160.0
150.0
140.0
130.0
162.8670
162.4664
141.6232
134.5578
134.1185
133.3974
130.4291
129.3760
128.8190
124.4962
X : parts per Million : 13C
Filename = H-T-Et-Th-Car-3.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = S#662792
Solvent = CHLOROFORM-D
Creation_time = 17-JUL-2008 03:28:05
Revision_time = 16-JUL-2008 20:45:34
Current_time = 2-NOV-2008 21:57:22
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 65536
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.0840448[s]
X_domain = 13C
X_freq = 125.76529768[MHz]
X_offset = 100[ppm]
X_points = 65536
X_prescans = 4
X_resolution = 0.47983613[Hz]
X_sweep = 31.44654088[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 1500
Total_scans = 1500
X_90_width = 14.2[us]
X_acq_time = 2.0840448[s]
X_angle = 30[deg]
X_pulse = 4.73333333[us]
Initial_wait = 1[s]
Noe_time = 1[s]
Phase_preset = 3[us]
Recvr_gain = 30
Relaxation_delay = 2[s]
Temp_get = 27.4[dC]
Unblank_time = 2[us]
EtO
O
S
S
O
EtO
104



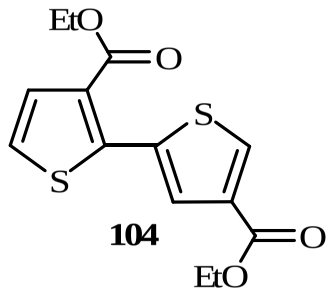
JEOL

```
Filename          = H-T-Et-Th-Car-3.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#662792
Solvent           = CHLOROFORM-D
Creation_time     = 17-JUL-2008 03:28:05
Revision_time     = 16-JUL-2008 20:45:34
Current_time      =  2-NOV-2008 22:51:46

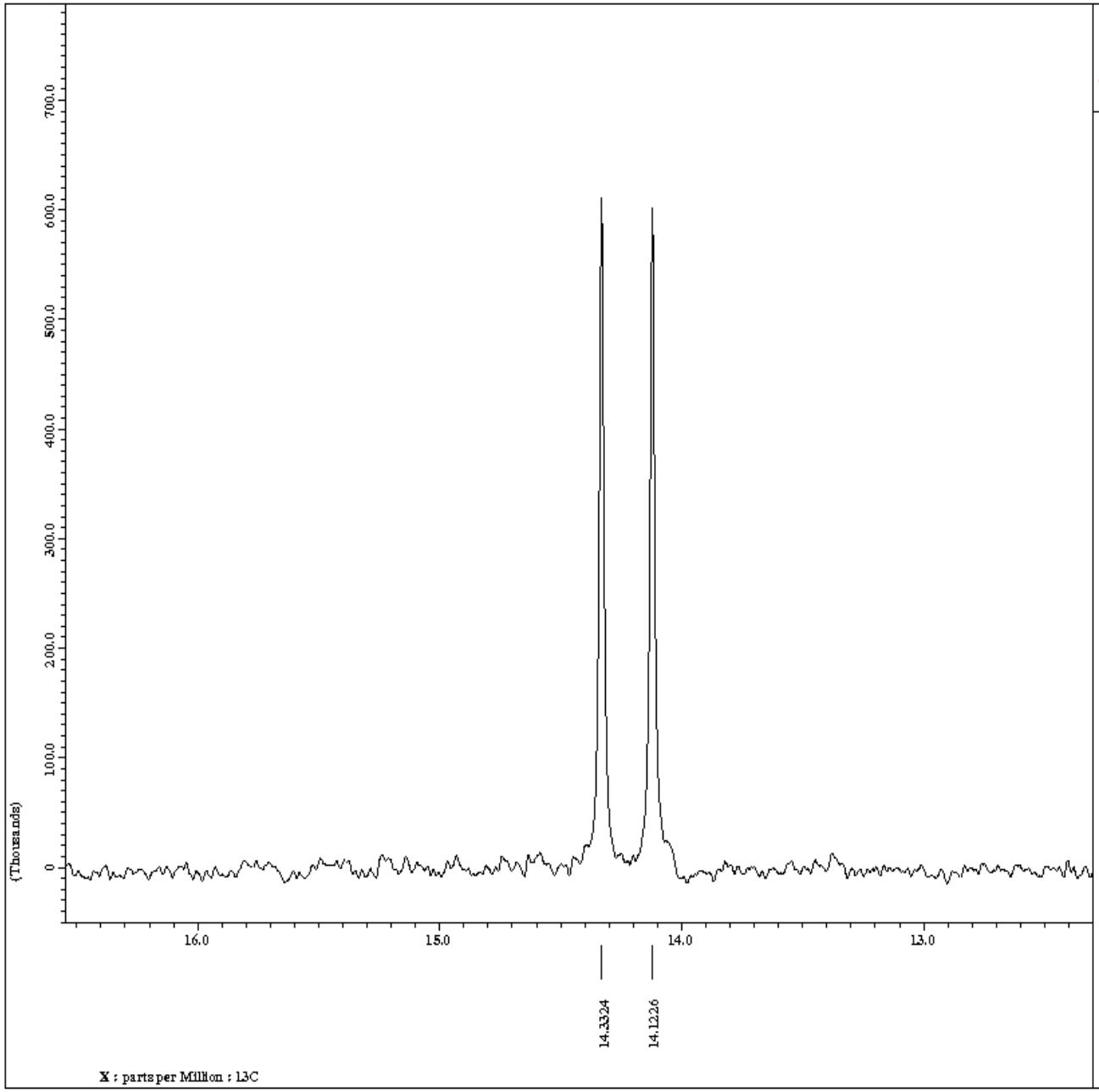
Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 65536
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 2.0840448[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 65536
X_prescans        = 4
X_resolution      = 0.47983613[Hz]
X_sweep           = 31.44654088[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 1500
Total_scans       = 1500

X_90_width        = 14.2[us]
X_acq_time        = 2.0840448[s]
X_angle           = 30[deg]
X_pulse           = 4.73333333[us]
Initial_wait      = 1[s]
Noe_time          = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 30
Relaxation_delay  = 2[s]
Temp_get          = 27.4[dC]
Unblank_time      = 2[us]
```



104



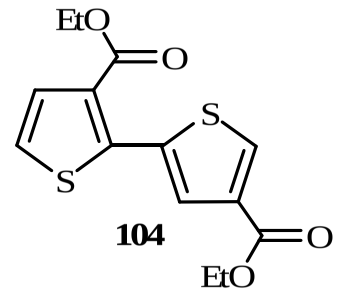
JEOL

```
Filename          = H-T-Et-Th-Car-3.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#662792
Solvent           = CHLOROFORM-D
Creation_time     = 17-JUL-2008 03:28:05
Revision_time     = 16-JUL-2008 20:45:34
Current_time      =  2-NOV-2008 22:01:30

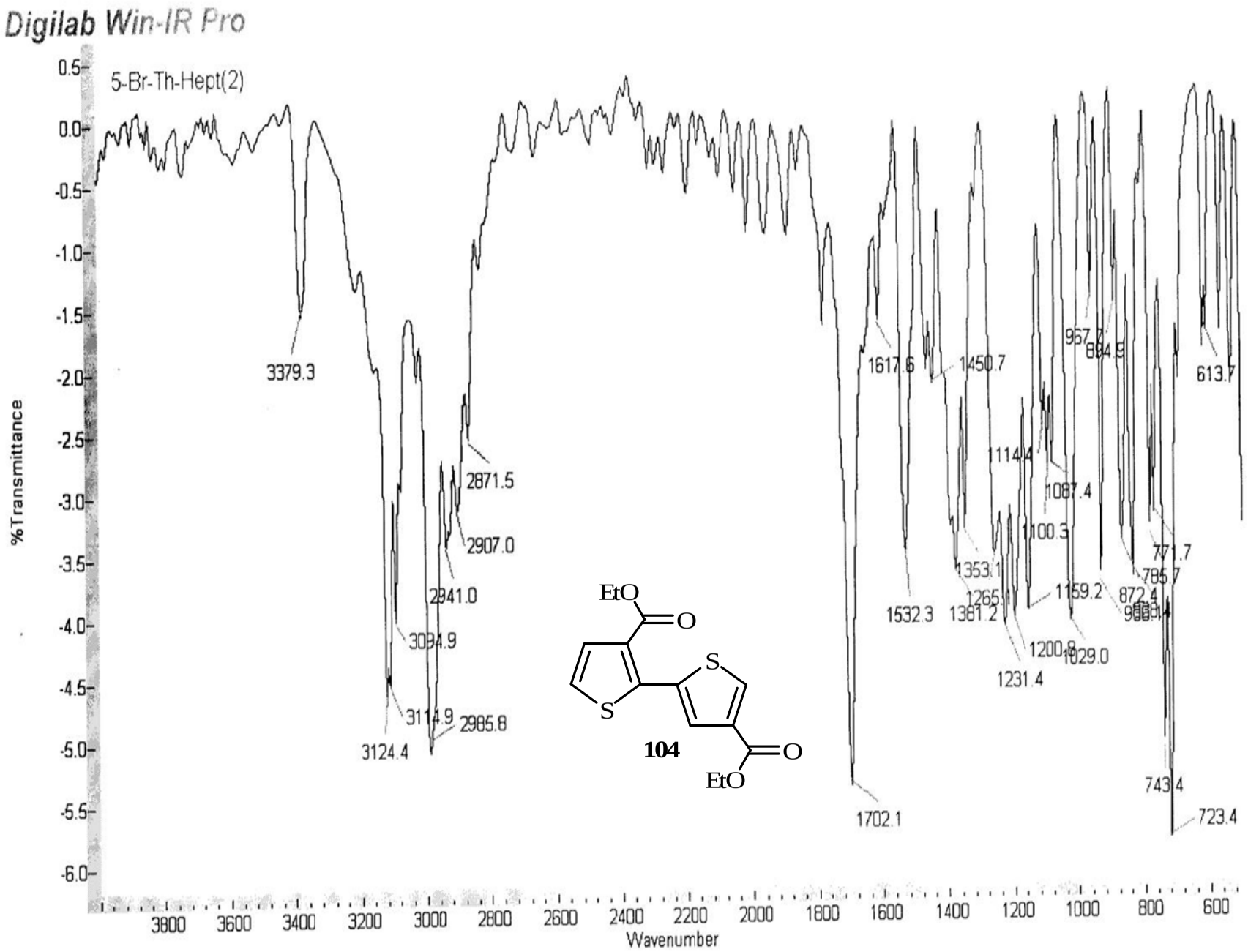
Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 65536
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

Field_strength    = 11.7473579[T]  (500[MH
X_acq_duration    = 2.0840448[s]
X_domain          = 13C
X_freq            = 125.76529760[MHz]
X_offset          = 100[ppm]
X_points          = 65536
X_prescans        = 4
X_resolution      = 0.47983613[Hz]
X_sweep           = 31.44654088[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 1500
Total_scans       = 1500

X_90_width        = 14.2[us]
X_acq_time        = 2.0840448[s]
X_angle           = 30[deg]
X_pulse           = 4.73333333[us]
Initial_wait      = 1[s]
Noe_time          = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 30
Relaxation_delay  = 2[s]
Temp_get          = 27.4[dC]
Unblank_time      = 2[us]
```

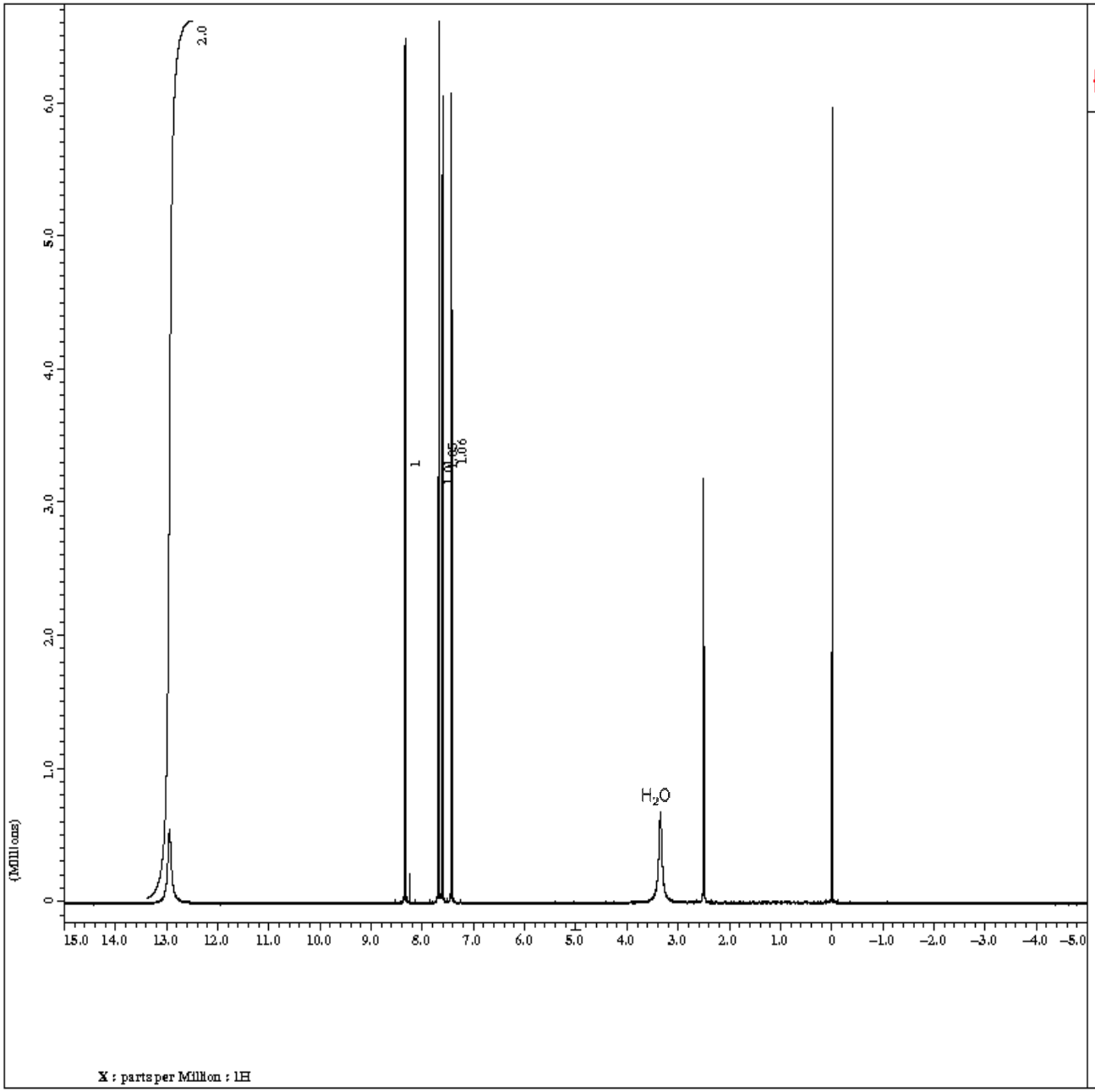


104

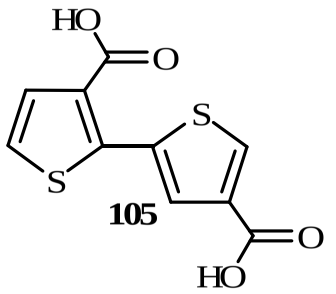

Digilab Win-IR Pro
5-Br-Th-Hept(2)
%Transmittance
Wavenumber
3379.3
3124.4
3114.9
3084.9
2985.8
2941.0
2907.0
2871.5
1702.1
1617.6
1532.3
1450.7
1381.2
1353.1
1265.1
1231.4
1200.8
1159.2
1114.4
1087.4
1029.0
967.7
884.9
872.4
785.7
771.7
743.4
723.4
613.7
EtO
O
S
S
O
EtO
104

APPENDIX 18

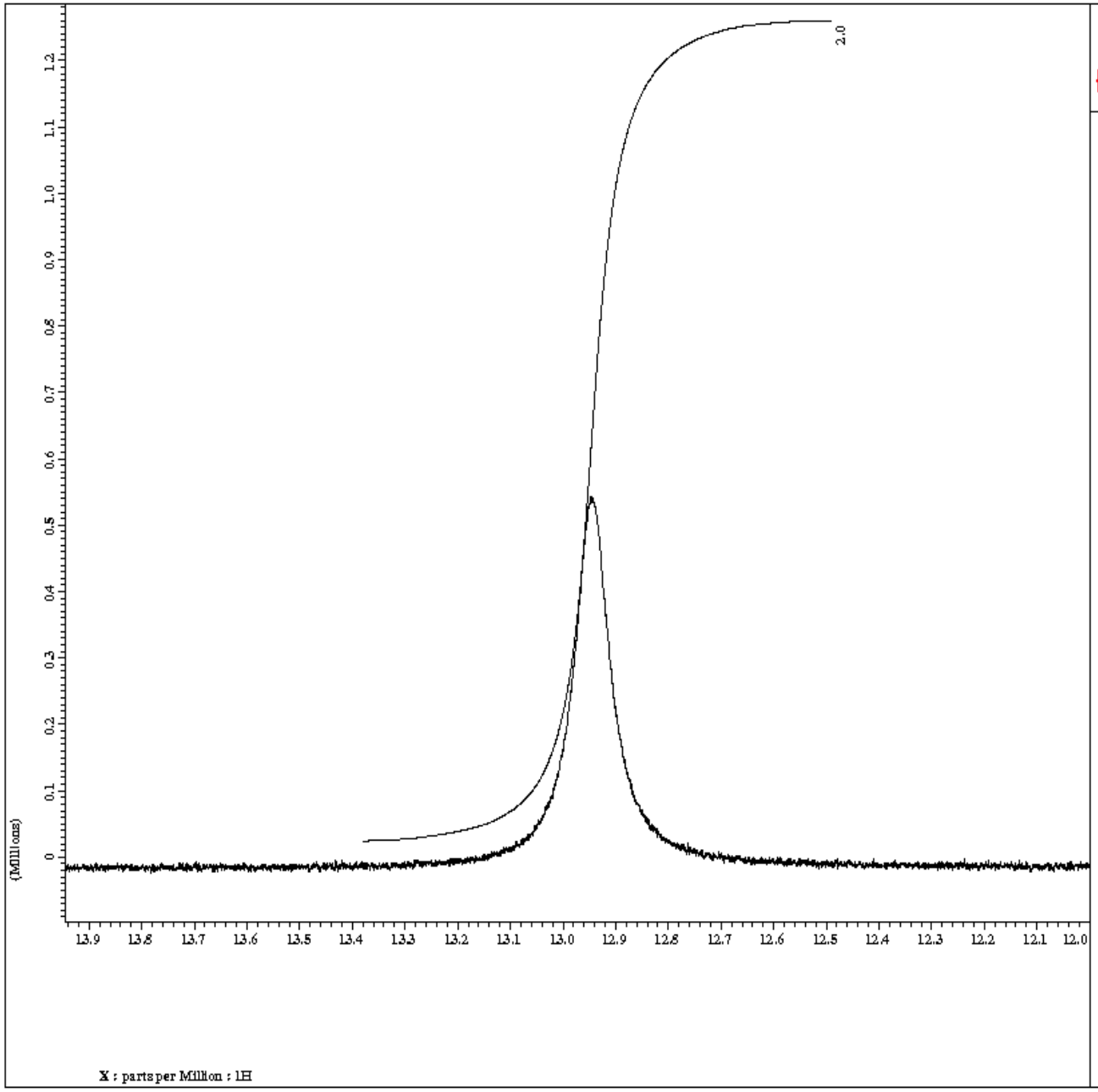
^{1}H, ^{13}C NMR and IR spectra of 2,2'-bithiophene-3,4-dicarboxylic acid (**105**)



Filename	= R-T-Th-Carb-Acid-4.jd
Author	= delta
Experiment	= single_pulse.exp
Sample_id	= S#703521
Solvent	= DMSO-D6
Creation_time	= 16-JUL-2008 04:47:59
Revision_time	= 6-NOV-2008 19:24:42
Current_time	= 6-NOV-2008 19:25:14
Comment	= Single Pulse Experime
Data_format	= 1D COMPLEX
Dim_size	= 65536
Dim_title	= 1H
Dim_units	= [ppm]
Dimensions	= X
Site	= Eclipse+ 500
Spectrometer	= DELTA_NMR
Field_strength	= 11.7473579[T] (500[MH
X_acq_duration	= 6.5470464[s]
X_domain	= 1H
X_freq	= 500.15991521[MHz]
X_offset	= 5[ppm]
X_points	= 65536
X_prescans	= 0
X_resolution	= 0.15274063[Hz]
X_sweep	= 10.01001001[kHz]
Clipped	= FALSE
Mod_return	= 1
Scans	= 15
Total_scans	= 15
X_90_width	= 10.5[us]
X_acq_time	= 6.5470464[s]
X_angle	= 45[deg]
X_pulse	= 9.25[us]
Initial_wait	= 1[s]
Phase_preset	= 3[us]
Recvr_gain	= 23
Relaxation_delay	= 14[s]
Temp_get	= 24.9[dC]
Unblank_time	= 2[us]



105

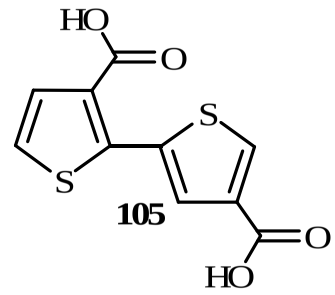



```
Filename          = H-T-Th-Carb-Acid-4.jd
Author            = delta
Experiment        = single_pulse.exp
Sample_id         = S#703521
Solvent           = DMSO-D6
Creation_time     = 18-JUL-2008 04:47:59
Revision_time     =  6-NOV-2008 19:27:47
Current_time      =  6-NOV-2008 19:28:00

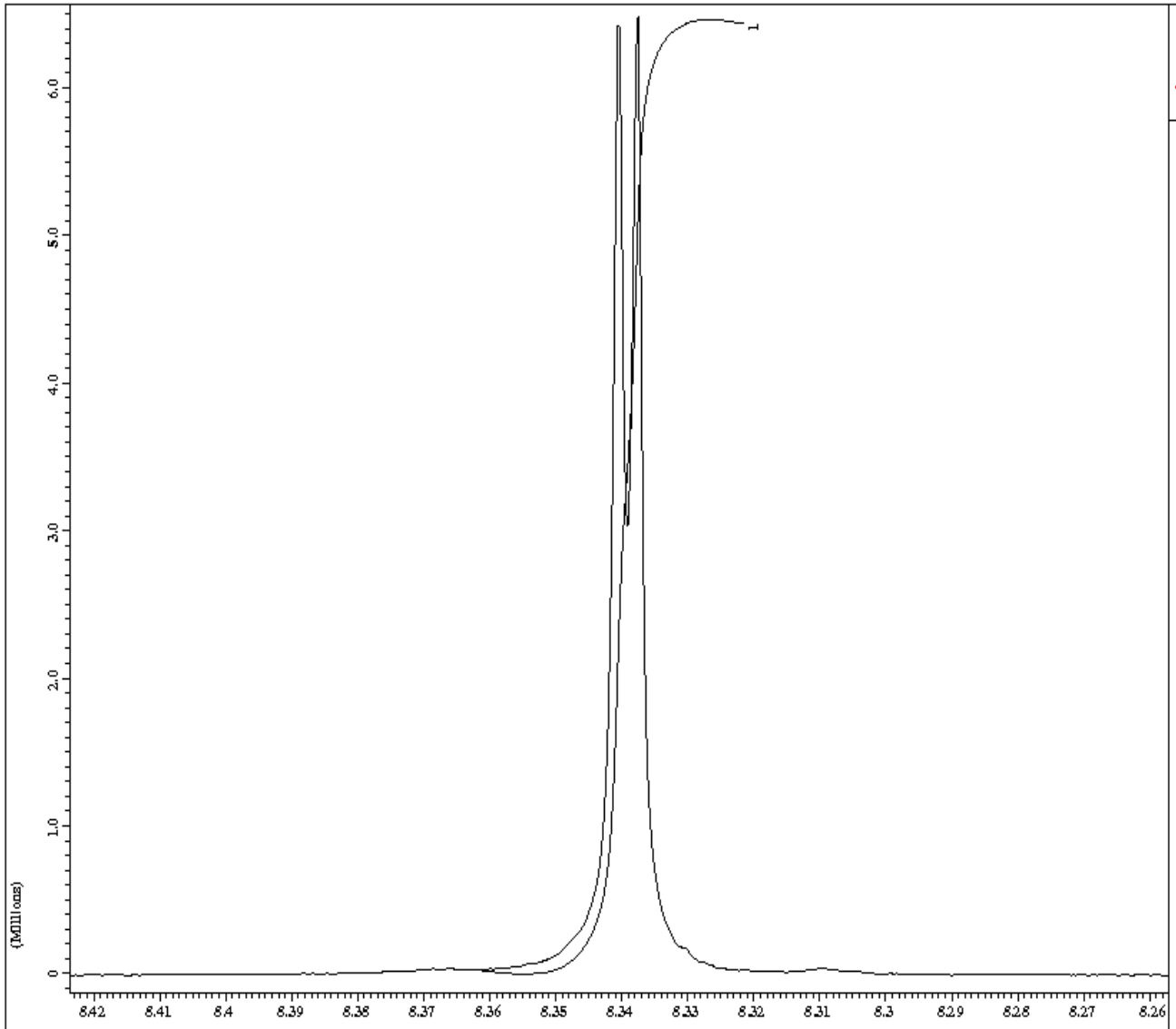
Comment           = Single Pulse Experime
Data_format       = 1D COMPLEX
Dim_size          = 65536
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

Field_strength    = 11.7473579[T]  (500[MH
X_acq_duration    = 6.5470464[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 5[ppm]
X_points          = 65536
X_prescans        = 0
X_resolution      = 0.15274063[Hz]
X_sweep           = 10.01001001[kHz]
Clipped           = FALSE
Mod_return        = 1
Scans             = 15
Total_scans       = 15

X_90_width        = 18.5[us]
X_acq_time        = 6.5470464[s]
X_angle           = 45[deg]
X_pulse           = 9.25[us]
Initial_wait      = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 23
Relaxation_delay  = 14[s]
Temp_get          = 24.9[dC]
Unblank_time      = 2[us]
```



105



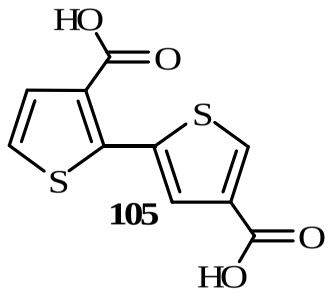
JEOL

```
Filename          = H-T-Th-Carb-Acid-4.jd
Author            = delta
Experiment        = single_pulse.exp
Sample_id         = S#703521
Solvent           = DMSO-D6
Creation_time     = 16-JUL-2008 04:47:59
Revision_time     =  6-NOV-2008 19:27:47
Current_time      =  6-NOV-2008 19:29:47

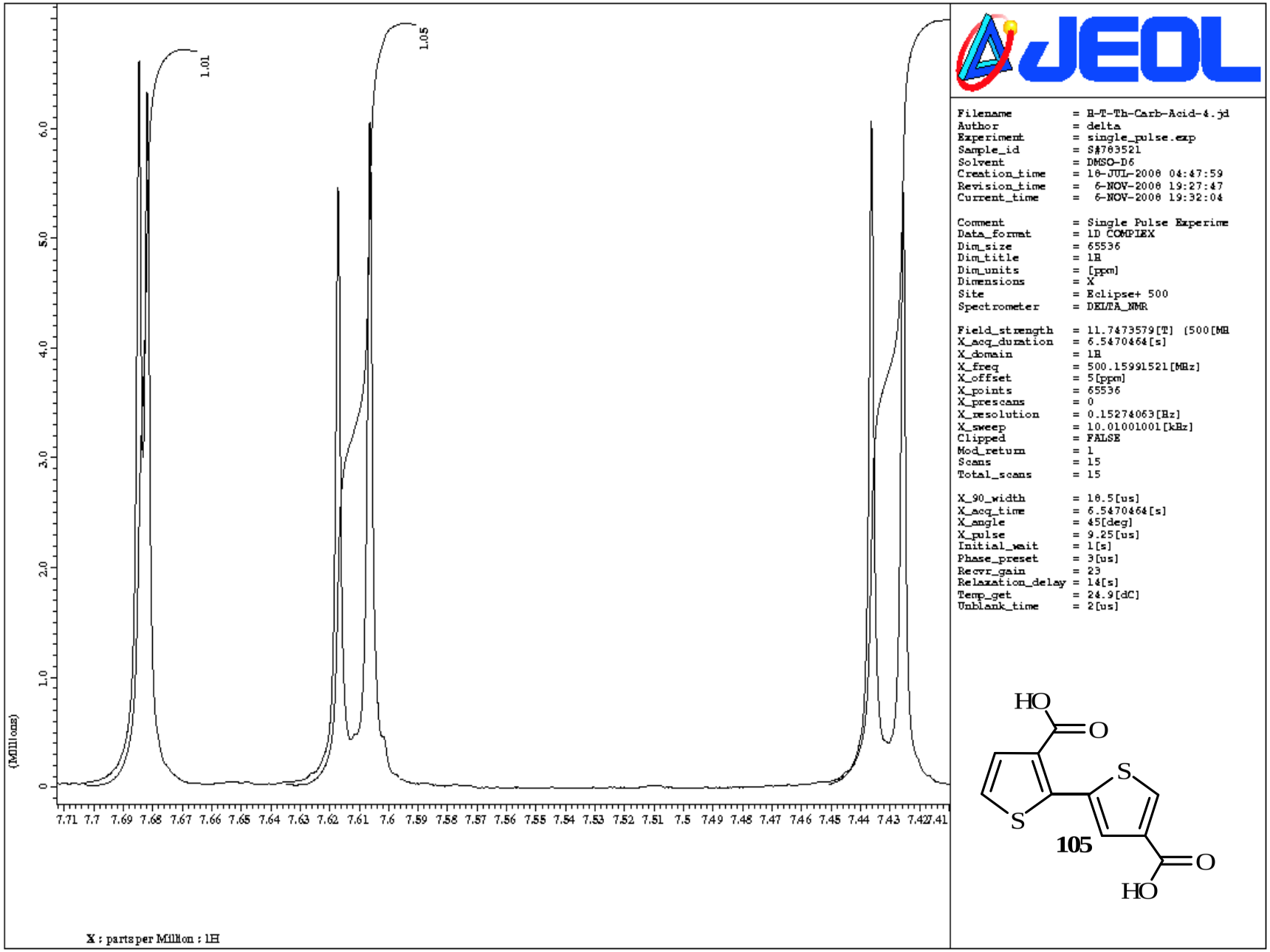
Comment           = Single Pulse Experime
Data_format       = 1D COMPLEX
Dim_size          = 65536
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

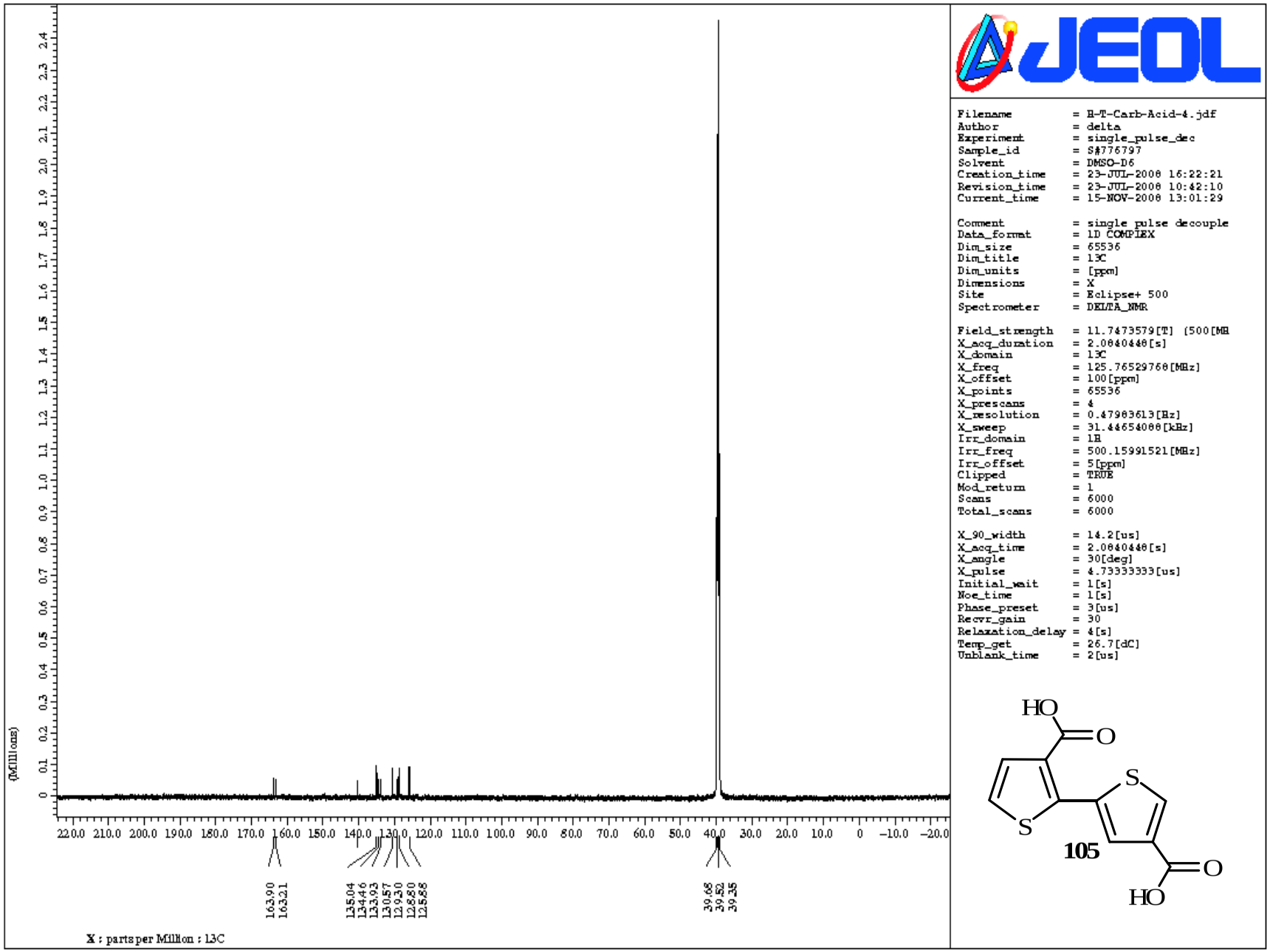
Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 6.5470464[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 5[ppm]
X_points          = 65536
X_prescans        = 0
X_resolution      = 0.1527#063[Hz]
X_sweep           = 10.01001001[kHz]
Clipped           = FALSE
Mod_return        = 1
Scans             = 15
Total_scans       = 15

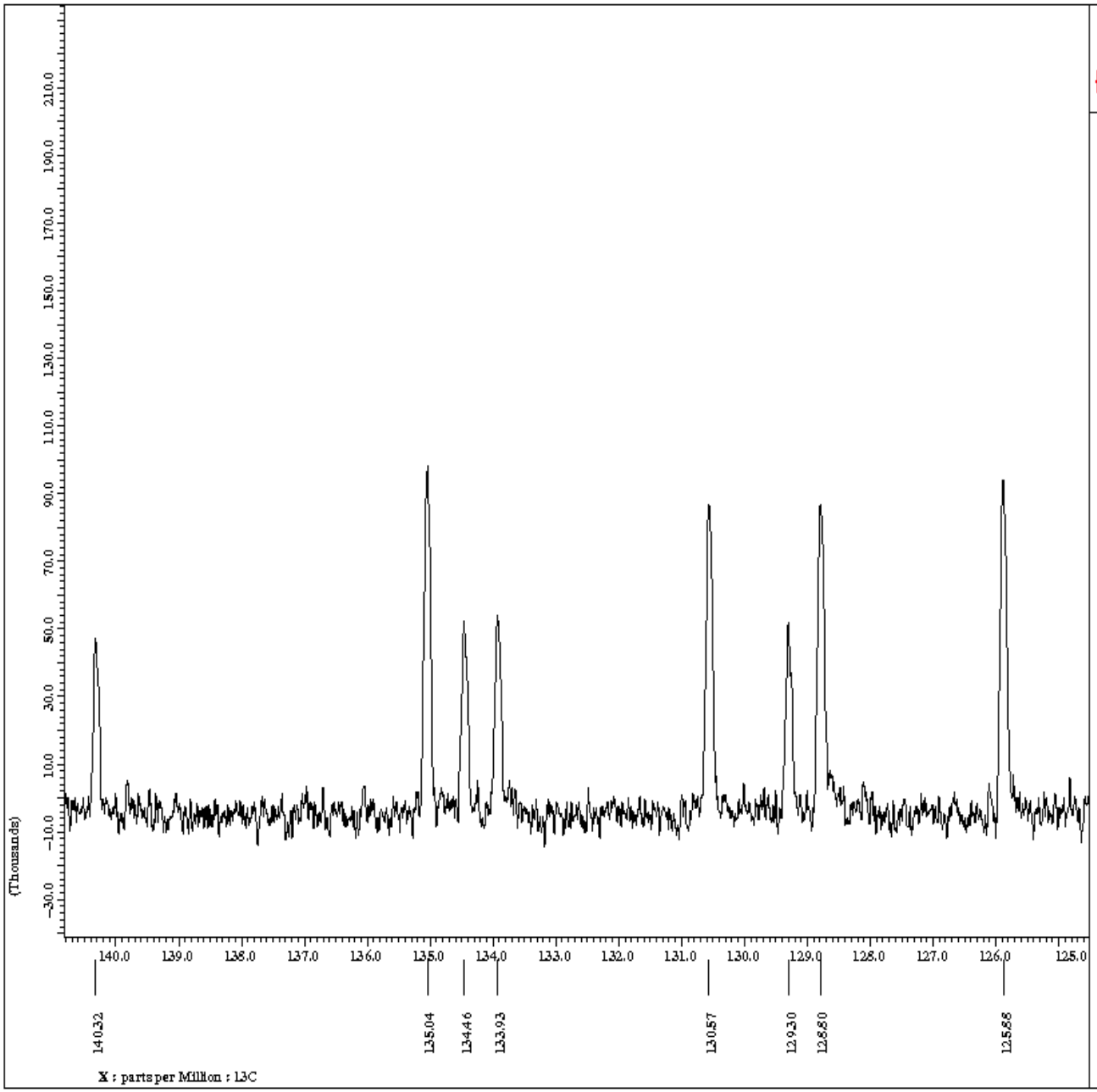
X_90_width        = 18.5[us]
X_acq_time        = 6.5470464[s]
X_angle           = 45[deg]
X_pulse           = 9.25[us]
Initial_wait      = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 23
Relaxation_delay  = 14[s]
Temp_get          = 24.9[dC]
Unblank_time      = 2[us]
```

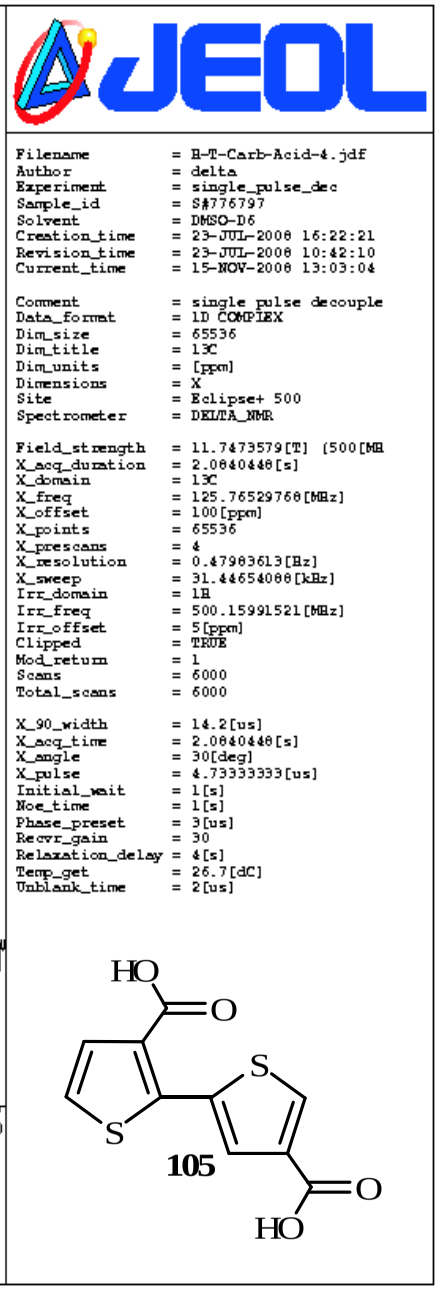


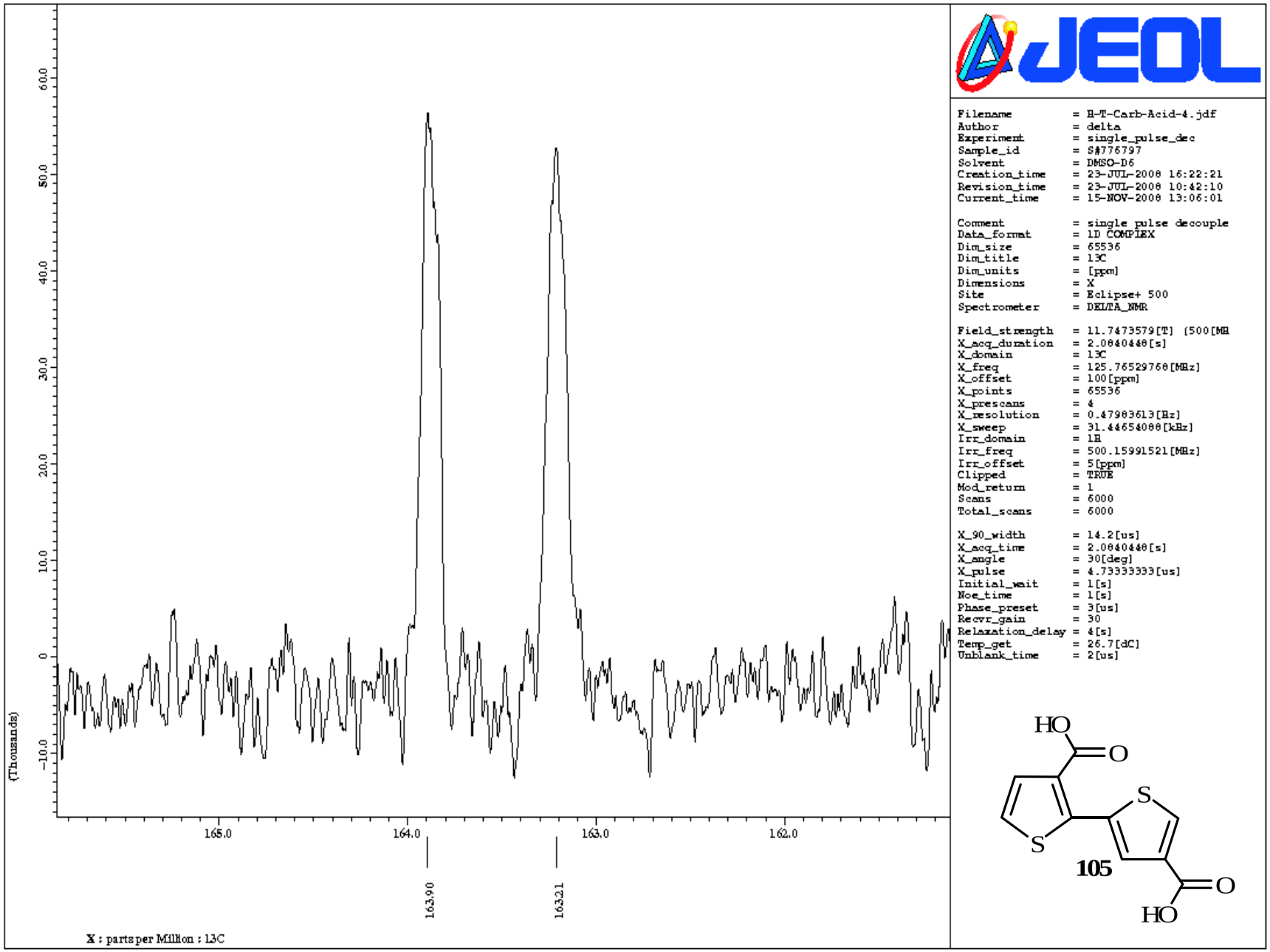
105


1.01
1.05
(Millions)
6.0
5.0
4.0
3.0
2.0
1.0
0
7.71 7.7 7.69 7.68 7.67 7.66 7.65 7.64 7.63 7.62 7.61 7.6 7.59 7.58 7.57 7.56 7.55 7.54 7.53 7.52 7.51 7.5 7.49 7.48 7.47 7.46 7.45 7.44 7.43 7.42 7.41
X : parts per Million : 1H
JEOL
Filename = H-T-Th-Carb-Acid-4.jd
Author = delta
Experiment = single_pulse.exp
Sample_id = S#703521
Solvent = DMSO-D6
Creation_time = 10-JUL-2008 04:47:59
Revision_time = 6-NOV-2008 19:27:47
Current_time = 6-NOV-2008 19:32:04
Comment = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 65536
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 6.5470464[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 65536
X_prescans = 0
X_resolution = 0.1527&063[Hz]
X_sweep = 10.01001001[kHz]
Clipped = FALSE
Mod_return = 1
Scans = 15
Total_scans = 15
X_90_width = 10.5[us]
X_acq_time = 6.5470464[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 23
Relaxation_delay = 14[s]
Temp_get = 24.9[dC]
Unblank_time = 2[us]
HO
O
S
S
105
O
HO


(Millions)
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
163.90
163.21
135.04
134.46
133.93
130.57
129.30
128.80
125.88
39.68
39.52
39.35
X : parts per Million : 13C
JEOL
Filename = H-T-Carb-Acid-4.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = S#776797
Solvent = DMSO-D6
Creation_time = 23-JUL-2008 16:22:21
Revision_time = 23-JUL-2008 10:42:10
Current_time = 15-NOV-2008 13:01:29
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 65536
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.0840448[s]
X_domain = 13C
X_freq = 125.76529768[MHz]
X_offset = 100[ppm]
X_points = 65536
X_prescans = 4
X_resolution = 0.47983613[Hz]
X_sweep = 31.44654088[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5[ppm]
Clipped = TRUE
Mod_return = 1
Scans = 6000
Total_scans = 6000
X_90_width = 14.2[us]
X_acq_time = 2.0840448[s]
X_angle = 30[deg]
X_pulse = 4.73333333[us]
Initial_wait = 1[s]
Noe_time = 1[s]
Phase_preset = 3[us]
Recvr_gain = 30
Relaxation_delay = 4[s]
Temp_get = 26.7[dC]
Unblank_time = 2[us]
HO
O
S
S
105
O
HO


(Thousands)
210.0
190.0
170.0
150.0
130.0
110.0
90.0
70.0
50.0
30.0
10.0
-10.0
-30.0
140.0
139.0
138.0
137.0
136.0
135.0
134.0
133.0
132.0
131.0
130.0
129.0
128.0
127.0
126.0
125.0
140.32
135.04
134.46
133.93
130.57
129.30
128.80
125.88
X : parts per Million : 13C


Filename = H-T-Carb-Acid-4.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = S#776797
Solvent = DMSO-D6
Creation_time = 23-JUL-2008 16:22:21
Revision_time = 23-JUL-2008 10:42:10
Current_time = 15-NOV-2008 13:03:04
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 65536
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.0840448[s]
X_domain = 13C
X_freq = 125.76529768[MHz]
X_offset = 100[ppm]
X_points = 65536
X_prescans = 4
X_resolution = 0.47983613[Hz]
X_sweep = 31.44654088[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5[ppm]
Clipped = TRUE
Mod_return = 1
Scans = 6000
Total_scans = 6000
X_90_width = 14.2[us]
X_acq_time = 2.0840448[s]
X_angle = 30[deg]
X_pulse = 4.73333333[us]
Initial_wait = 1[s]
Noe_time = 1[s]
Phase_preset = 3[us]
Recvr_gain = 30
Relaxation_delay = 4[s]
Temp_get = 26.7[dC]
Unblank_time = 2[us]
HO
O
S
S
105
O
HO



JEOL

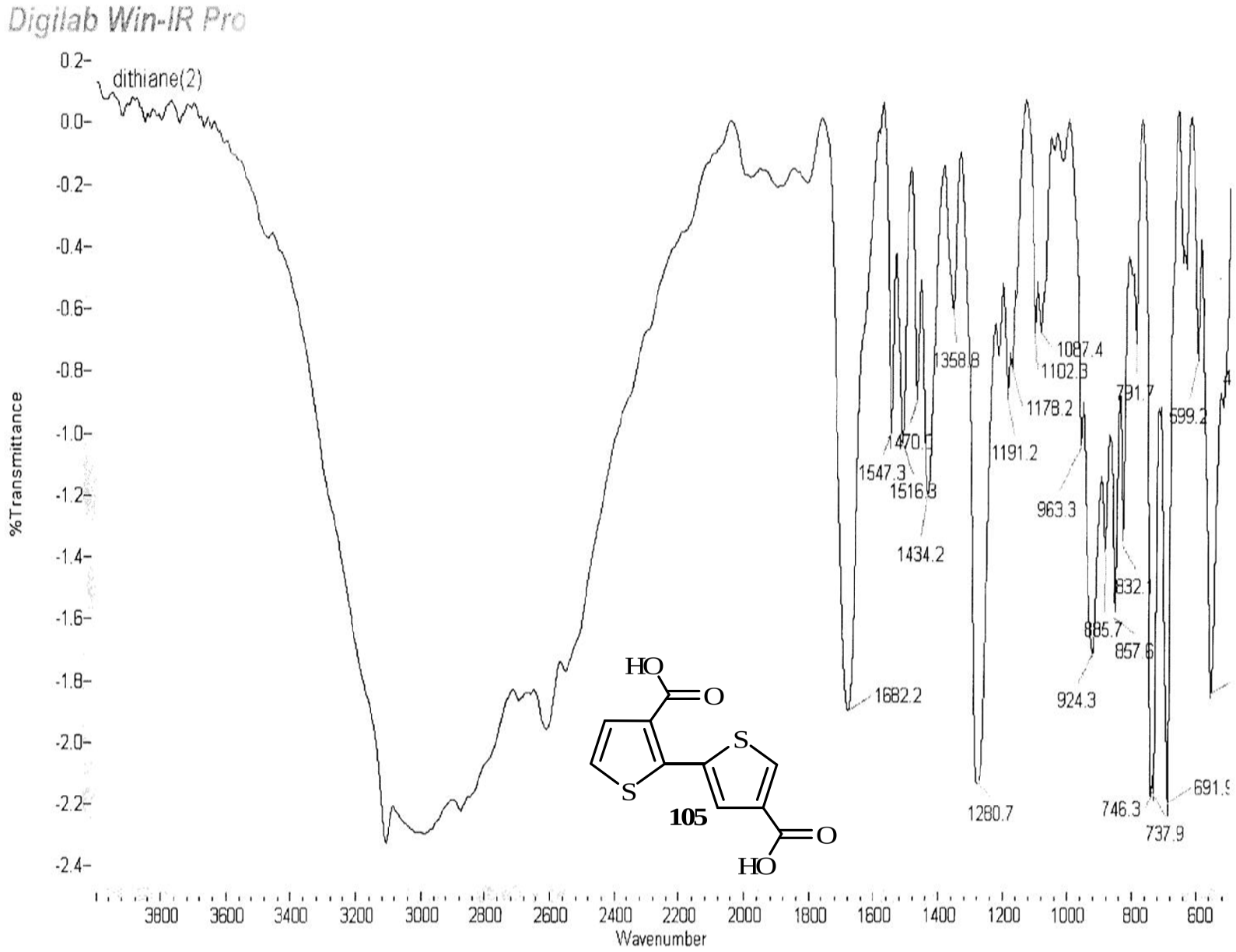
```
Filename          = B-T-Carb-Acid-4.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#776797
Solvent           = DMSO-D6
Creation_time     = 23-JUL-2008 16:22:21
Revision_time     = 23-JUL-2008 10:42:10
Current_time      = 15-NOV-2008 13:06:01

Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 65536
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 2.0840448[s]
X_domain          = 13C
X_freq            = 125.76529760[MHz]
X_offset          = 100[ppm]
X_points          = 65536
X_prescans        = 4
X_resolution      = 0.47983613[Hz]
X_sweep           = 31.44654088[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5[ppm]
Clipped           = TRUE
Mod_return        = 1
Scans             = 6000
Total_scans       = 6000

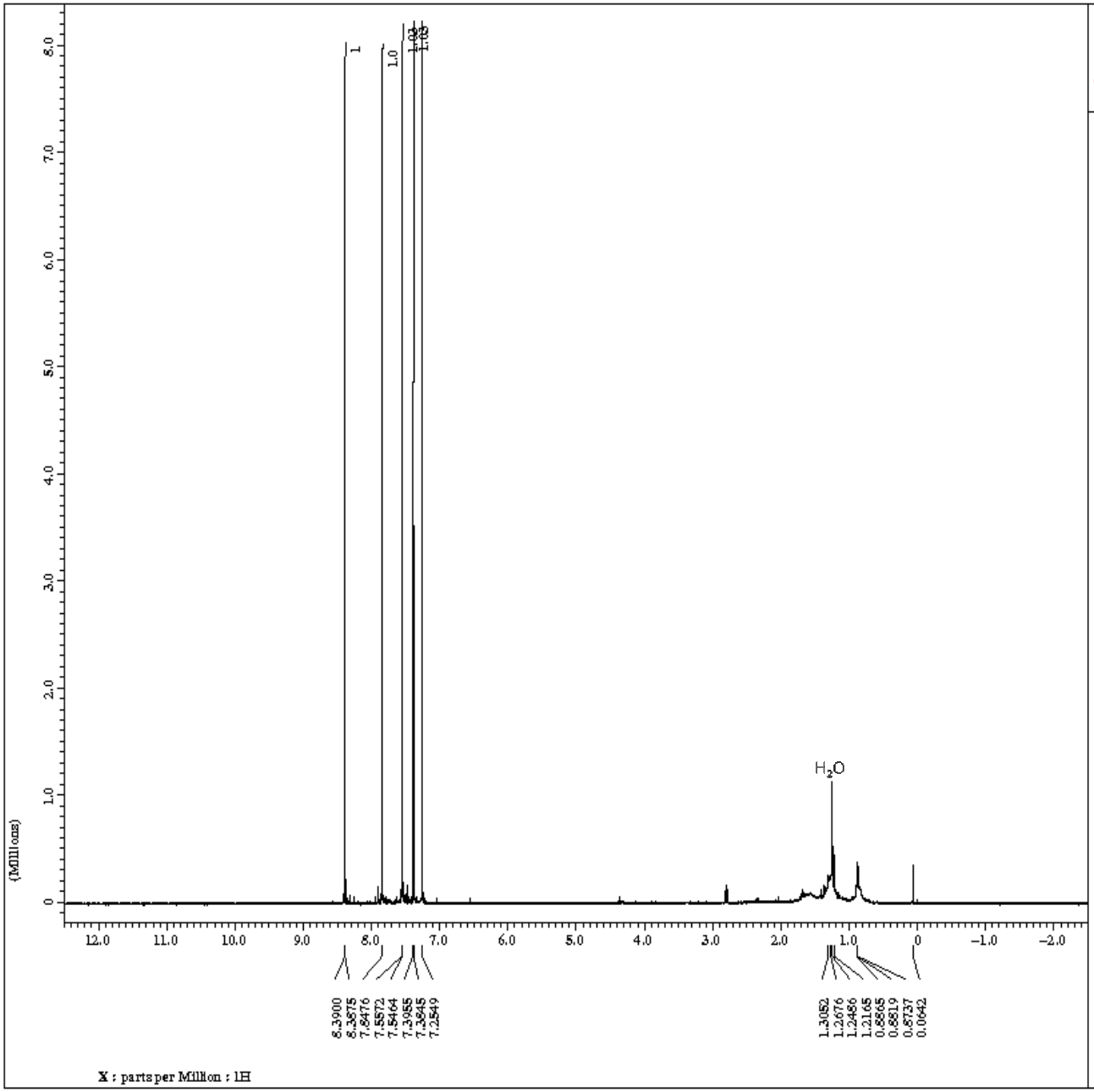
X_90_width        = 14.2[us]
X_acq_time        = 2.0840448[s]
X_angle           = 30[deg]
X_pulse           = 4.73333333[us]
Initial_wait      = 1[s]
Noe_time          = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 30
Relaxation_delay  = 4[s]
Temp_get          = 26.7[dC]
Unblank_time      = 2[us]
```


105


Digilab Win-IR Pro
dithiane(2)
%Transmittance
Wavenumber
0.2
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
-1.4
-1.6
-1.8
-2.0
-2.2
-2.4
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
1682.2
1547.3
1516.8
1470.5
1434.2
1358.8
1280.7
1191.2
1178.2
1102.3
1087.4
963.3
924.3
885.7
857.6
832.1
791.7
746.3
737.9
691.9
599.2
HO
O
S
S
O
HO
105

APPENDIX 19

^{1}H, ^{19}F NMR and IR spectra of 2,2'-bithiophene-3,4'-dicarbonyl difluoride (**98**)

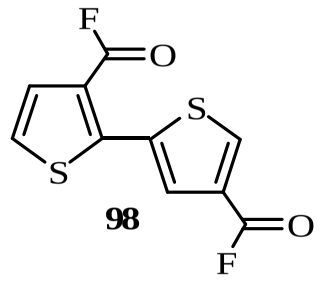


Filename = Acid-F-5.jdf
Author = delta
Experiment = single_pulse.exp
Sample_id = S#047366
Solvent = CHLOROFORM-D
Creation_time = 25-JUL-2008 06:36:21
Revision_time = 24-JUL-2008 23:43:51
Current_time = 3-NOV-2008 13:55:06

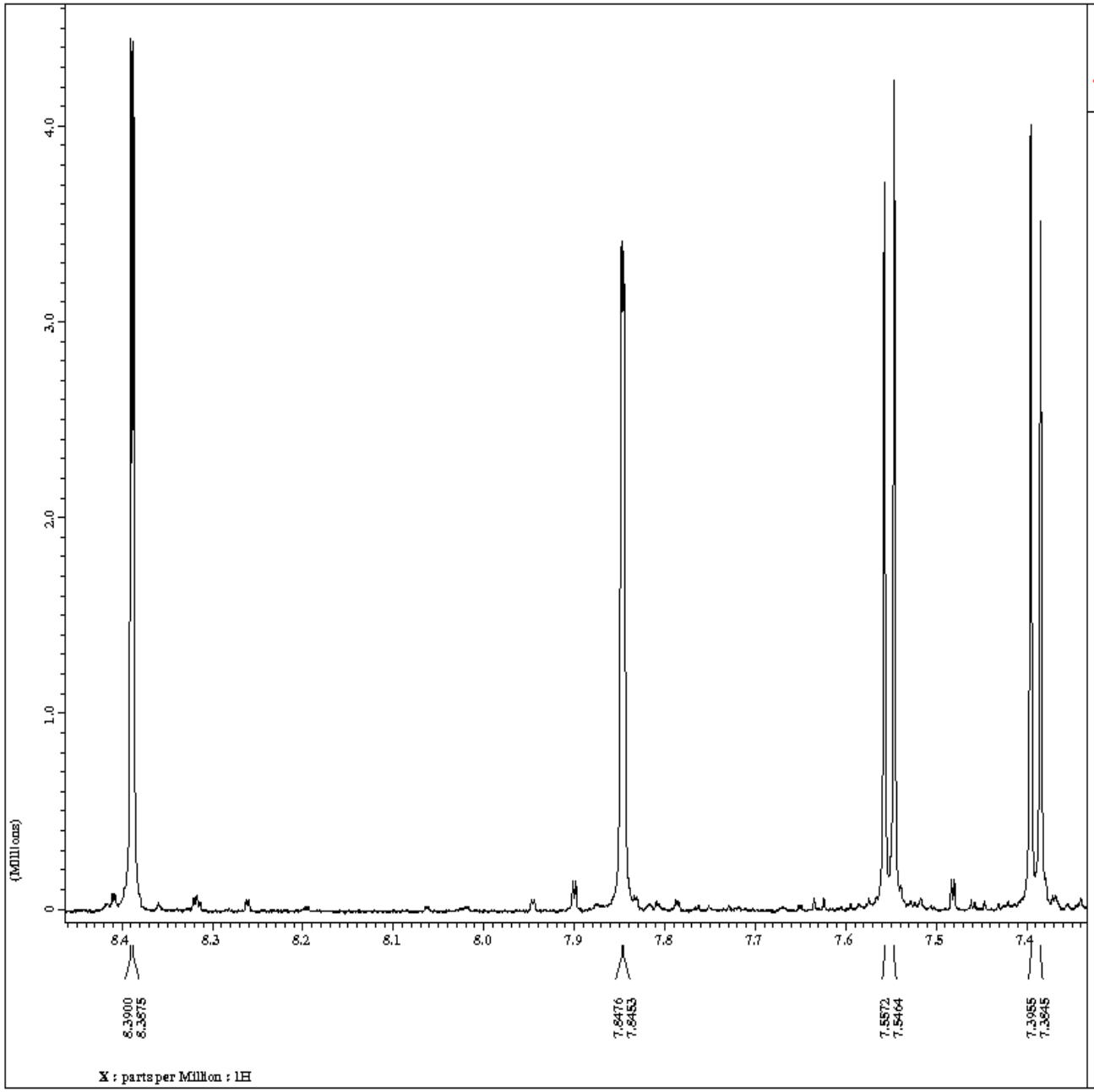
Comment = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 65536
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR

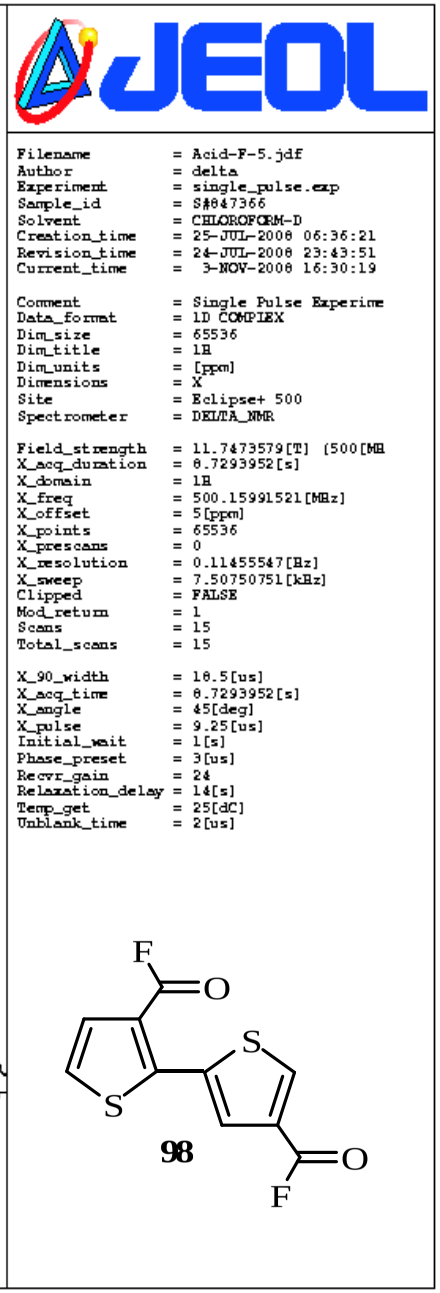
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 0.7293952[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 65536
X_prescans = 0
X_resolution = 0.11455547[Hz]
X_sweep = 7.50750751[kHz]
Clipped = FALSE
Mod_return = 1
Scans = 15
Total_scans = 15

X_90_width = 18.5[us]
X_acq_time = 0.7293952[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 24
Relaxation_delay = 14[s]
Temp_get = 25[dC]
Unblank_time = 2[us]



98





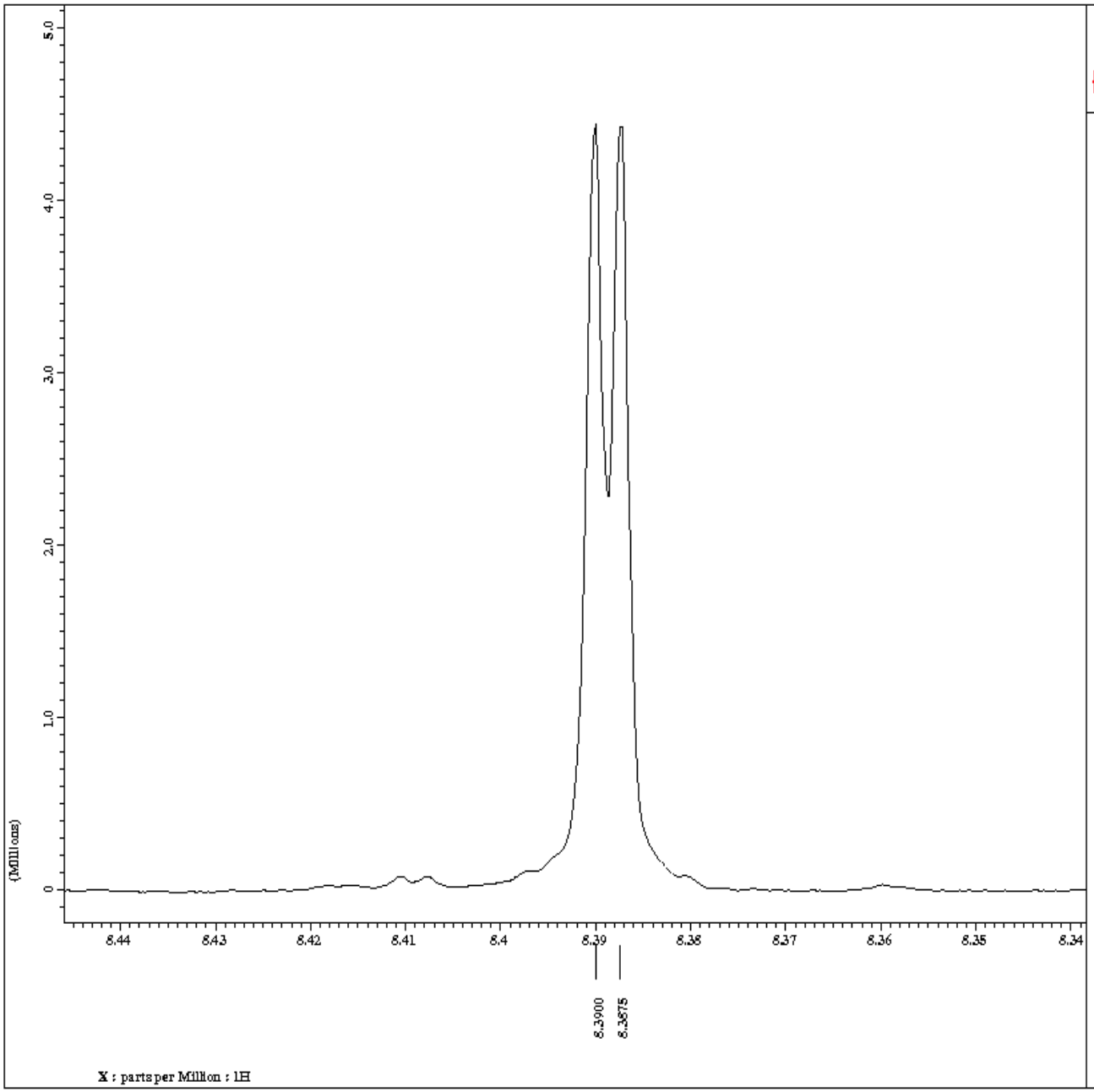

```
Filename          = Acid-F-5.jdf
Author            = delta
Experiment        = single_pulse.exp
Sample_id         = S#047366
Solvent           = CHLOROFORM-D
Creation_time     = 25-JUL-2008 06:36:21
Revision_time     = 24-JUL-2008 23:43:51
Current_time      =  3-NOV-2008 16:30:19

Comment           = Single Pulse Experime
Data_format       = 1D COMPLEX
Dim_size          = 65536
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 0.7293952[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 5[ppm]
X_points          = 65536
X_prescans        = 0
X_resolution      = 0.11455547[Hz]
X_sweep           = 7.50750751[kHz]
Clipped           = FALSE
Mod_return        = 1
Scans             = 15
Total_scans       = 15

X_90_width        = 10.5[us]
X_acq_time        = 0.7293952[s]
X_angle           = 45[deg]
X_pulse           = 9.25[us]
Initial_wait      = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 24
Relaxation_delay  = 14[s]
Temp_get          = 25[dC]
Unblank_time      = 2[us]
```


98



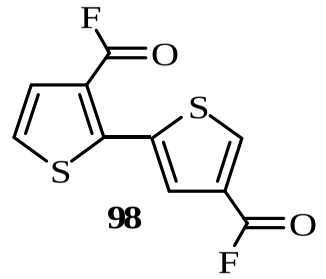
JEOL

```
Filename          = Acid-F-5.jdf
Author            = delta
Experiment        = single_pulse.exp
Sample_id         = S#847366
Solvent           = CHLOROFORM-D
Creation_time     = 25-JUL-2008 06:36:21
Revision_time     = 24-JUL-2008 23:43:51
Current_time      =  3-NOV-2008 13:58:27

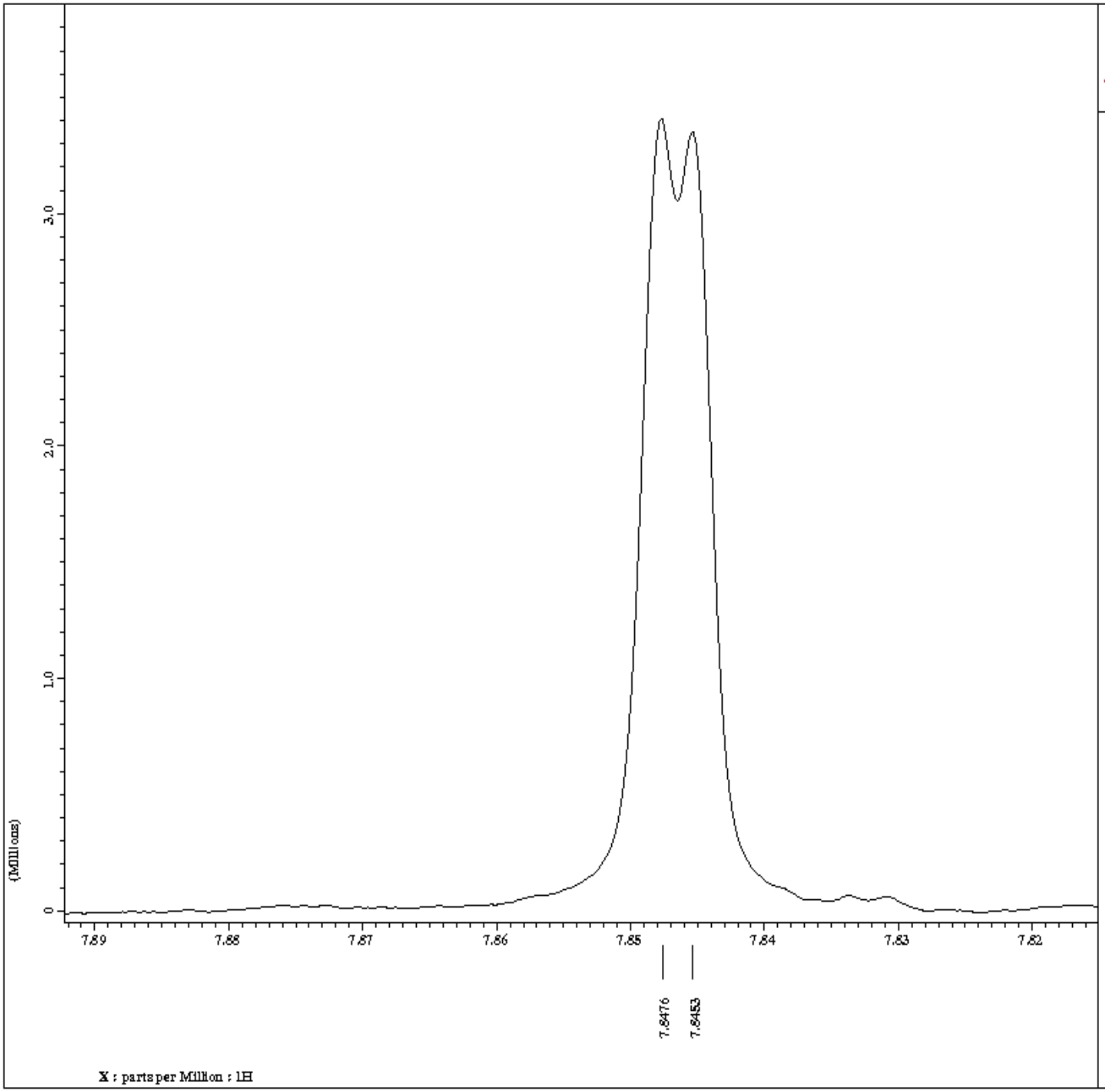
Comment           = Single Pulse Experime
Data_format       = 1D COMPLEX
Dim_size          = 65536
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 0.7293952[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 5[ppm]
X_points          = 65536
X_prescans        = 0
X_resolution      = 0.11455547[Hz]
X_sweep           = 7.50750751[kHz]
Clipped           = FALSE
Mod_return        = 1
Scans             = 15
Total_scans       = 15

X_90_width        = 10.5[us]
X_acq_time        = 0.7293952[s]
X_angle           = 45[deg]
X_pulse           = 9.25[us]
Initial_wait      = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 24
Relaxation_delay  = 14[s]
Temp_get          = 25[dC]
Unblank_time      = 2[us]
```



98



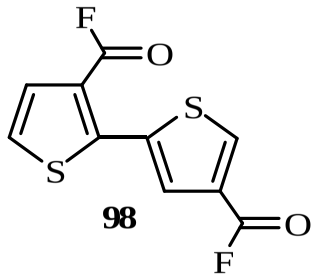
JEOL

```
Filename          = Acid-F-5.jdf
Author            = delta
Experiment        = single_pulse.exp
Sample_id         = S#847366
Solvent           = CHLOROFORM-D
Creation_time     = 25-JUL-2008 06:36:21
Revision_time     = 24-JUL-2008 23:43:51
Current_time      =  3-NOV-2008 16:25:39

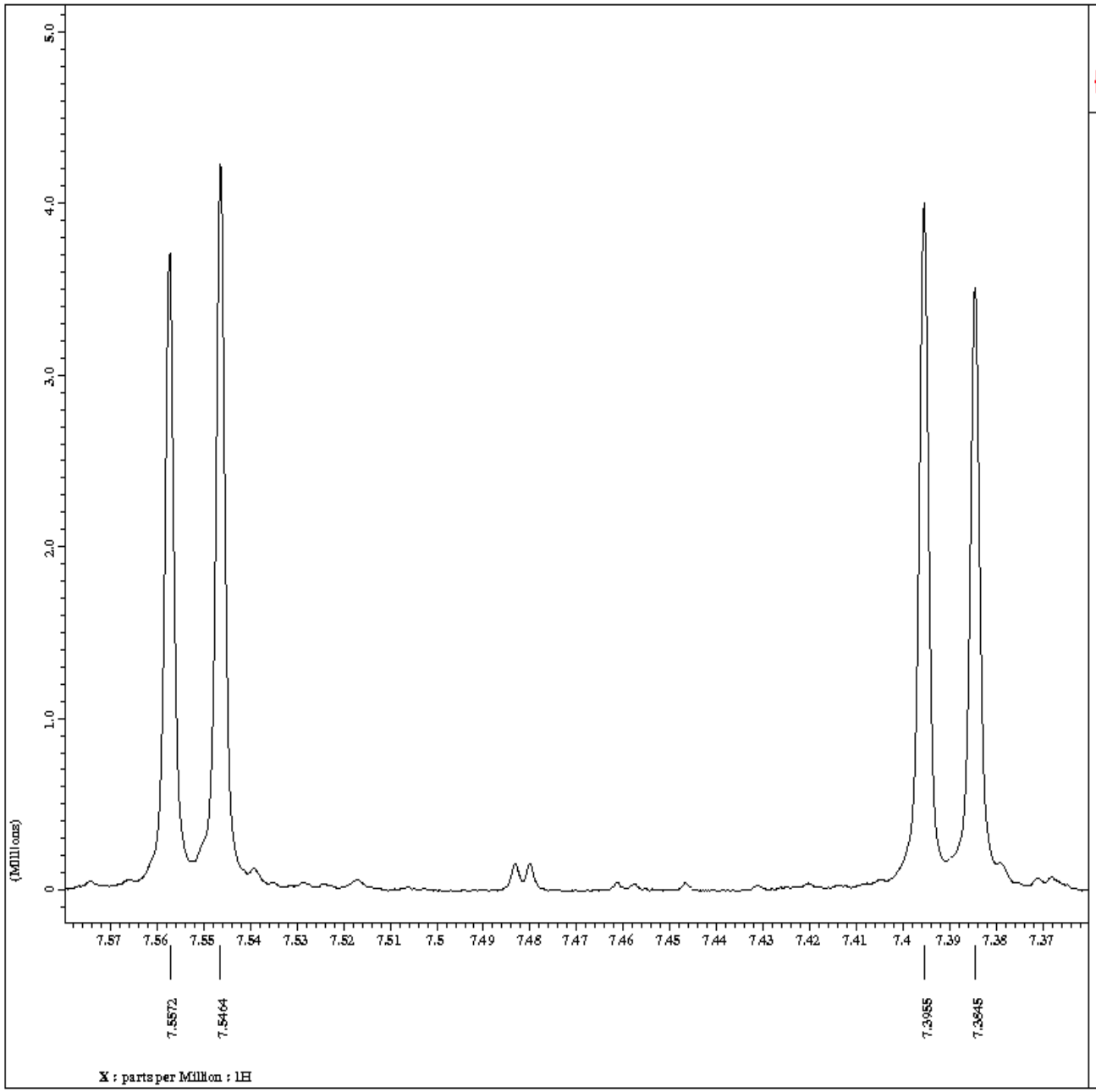
Comment           = Single Pulse Experime
Data_format       = 1D COMPLEX
Dim_size          = 65536
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 0.7293952[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 5[ppm]
X_points          = 65536
X_prescans        = 0
X_resolution      = 0.11455547[Hz]
X_sweep           = 7.50750751[kHz]
Clipped           = FALSE
Mod_return        = 1
Scans             = 15
Total_scans       = 15

X_90_width        = 10.5[us]
X_acq_time        = 0.7293952[s]
X_angle           = 45[deg]
X_pulse           = 9.25[us]
Initial_wait      = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 24
Relaxation_delay  = 14[s]
Temp_get          = 25[dC]
Unblank_time      = 2[us]
```



98



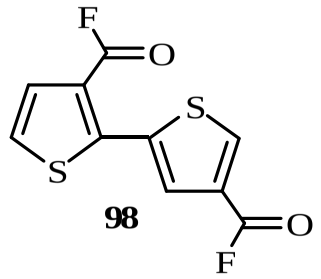
JEOL

```
Filename          = Acid-F-5.jdf
Author            = delta
Experiment        = single_pulse.exp
Sample_id         = S#047366
Solvent           = CHLOROFORM-D
Creation_time     = 25-JUL-2008 06:36:21
Revision_time     = 24-JUL-2008 23:43:51
Current_time      =  3-NOV-2008 16:27:49

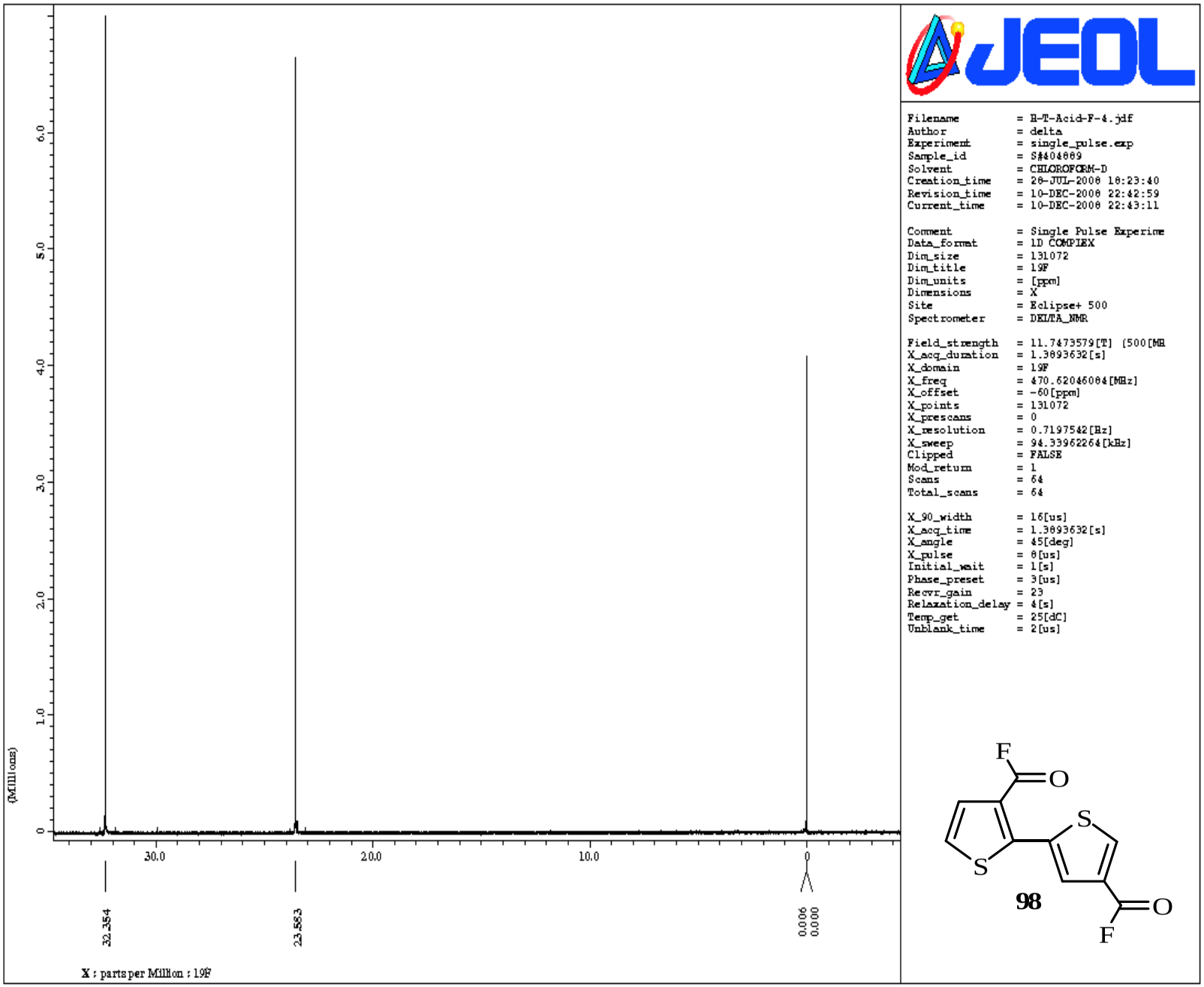
Comment           = Single Pulse Experime
Data_format       = 1D COMPLEX
Dim_size          = 65536
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

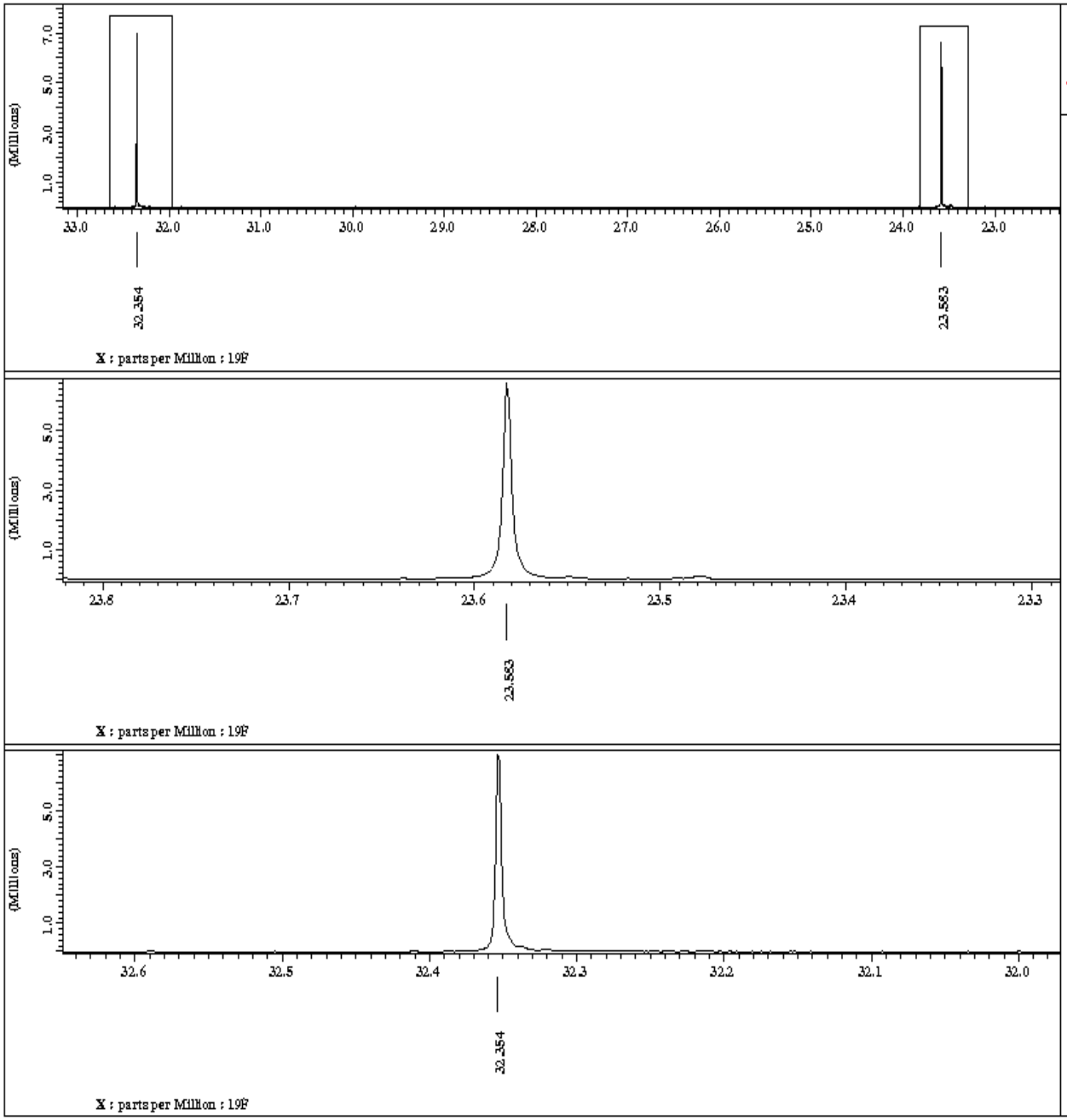
Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 0.7293952[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 5[ppm]
X_points          = 65536
X_prescans        = 0
X_resolution      = 0.11455547[Hz]
X_sweep           = 7.50750751[kHz]
Clipped           = FALSE
Mod_return        = 1
Scans             = 15
Total_scans       = 15

X_90_width        = 10.5[us]
X_acq_time        = 0.7293952[s]
X_angle           = 45[deg]
X_pulse           = 9.25[us]
Initial_wait      = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 24
Relaxation_delay  = 14[s]
Temp_get          = 25[dC]
Unblank_time      = 2[us]
```



98


(Millions)
6.0
5.0
4.0
3.0
2.0
1.0
0
30.0
20.0
10.0
0
-23.354
-23.583
0.006
0.000
X : parts per Million : 19F
Filename = H-T-Acid-F-4.jdf
Author = delta
Experiment = single_pulse.exp
Sample_id = S#404869
Solvent = CHLOROFORM-D
Creation_time = 28-JUL-2008 18:23:40
Revision_time = 10-DEC-2008 22:42:59
Current_time = 10-DEC-2008 22:43:11
Comment = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 131072
Dim_title = 19F
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 1.3893632[s]
X_domain = 19F
X_freq = 470.62046064[MHz]
X_offset = -60[ppm]
X_points = 131072
X_prescans = 0
X_resolution = 0.7197542[Hz]
X_sweep = 94.33962264[kHz]
Clipped = FALSE
Mod_return = 1
Scans = 64
Total_scans = 64
X_90_width = 16[us]
X_acq_time = 1.3893632[s]
X_angle = 45[deg]
X_pulse = 8[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 23
Relaxation_delay = 4[s]
Temp_get = 25[dC]
Unblank_time = 2[us]
F
O
S
S
O
F
98



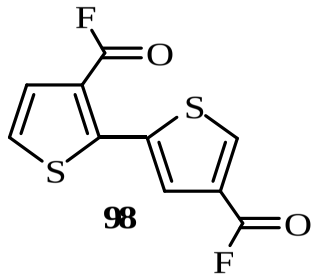
JEOL

```
Filename          = H-T-Acid-F-4.jdf
Author            = delta
Experiment        = single_pulse.exp
Sample_id         = S#404089
Solvent           = CHLOROFORM-D
Creation_time     = 26-JUL-2008 18:23:40
Revision_time     = 10-DEC-2008 22:42:59
Current_time      = 10-DEC-2008 22:44:45

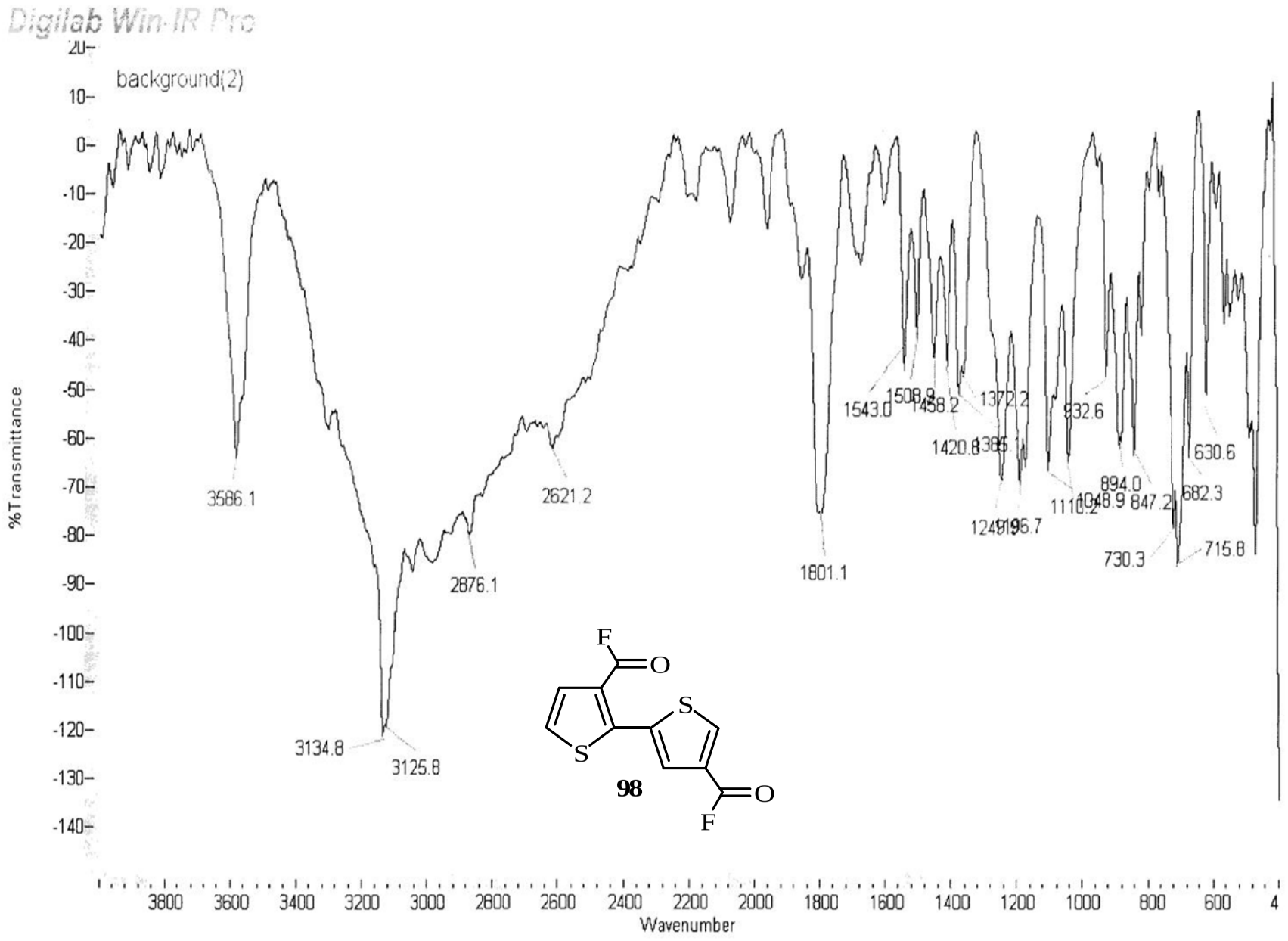
Comment           = Single Pulse Experime
Data_format       = 1D COMPLEX
Dim_size          = 131072
Dim_title         = 19F
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 1.3893632[s]
X_domain          = 19F
X_freq            = 470.62046084[MHz]
X_offset          = -60[ppm]
X_points          = 131072
X_prescans        = 0
X_resolution      = 0.7197542[Hz]
X_sweep           = 94.33962264[kHz]
Clipped           = FALSE
Mod_return        = 1
Scans             = 64
Total_scans       = 64

X_90_width        = 16[us]
X_acq_time        = 1.3893632[s]
X_angle           = 45[deg]
X_pulse           = 8[us]
Initial_wait      = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 23
Relaxation_delay  = 4[s]
Temp_get          = 25[dC]
Unblank_time      = 2[us]
```



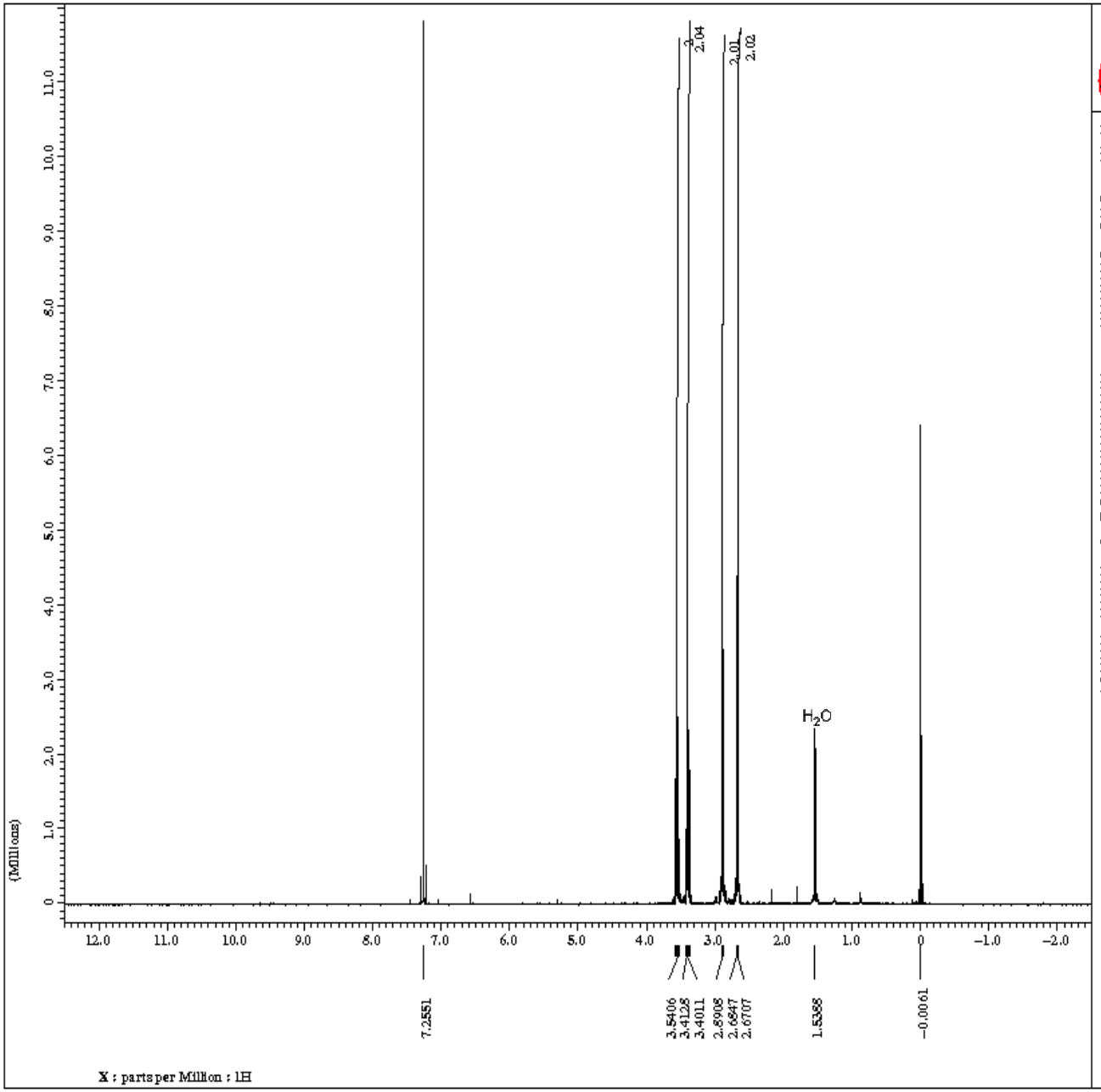
98


Digilab Win-IR Pro
background(2)
%Transmittance
Wavenumber
3586.1
3134.8
3125.8
2876.1
2621.2
1801.1
1543.0
1508.8
1458.2
1420.8
1372.2
1249.9
1196.7
1110.2
1048.9
932.6
894.0
847.2
730.3
715.8
682.3
630.6
F
O
S
S
O
F

98

APPENDIX 20

^{1}H, ^{13}C NMR and IR spectra of spiro[1,3-dithiolane]-2,4'-1',3'-dichloro-5',6'-dihydro-cyclopenta[*c*]thiophene (**143**)



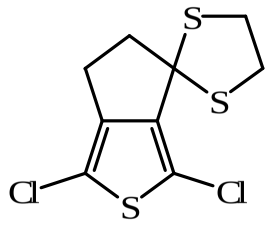
JEOL

```
Filename          = Dithilane -pent-cyc-t
Author            = delta
Experiment        = single_pulse.exp
Sample_id         = S#457275
Solvent           = CHLOROFORM-D
Creation_time     =  1-FEB-2006 15:04:24
Revision_time     =  4-NOV-2008 12:37:56
Current_time      =  4-NOV-2008 12:38:19

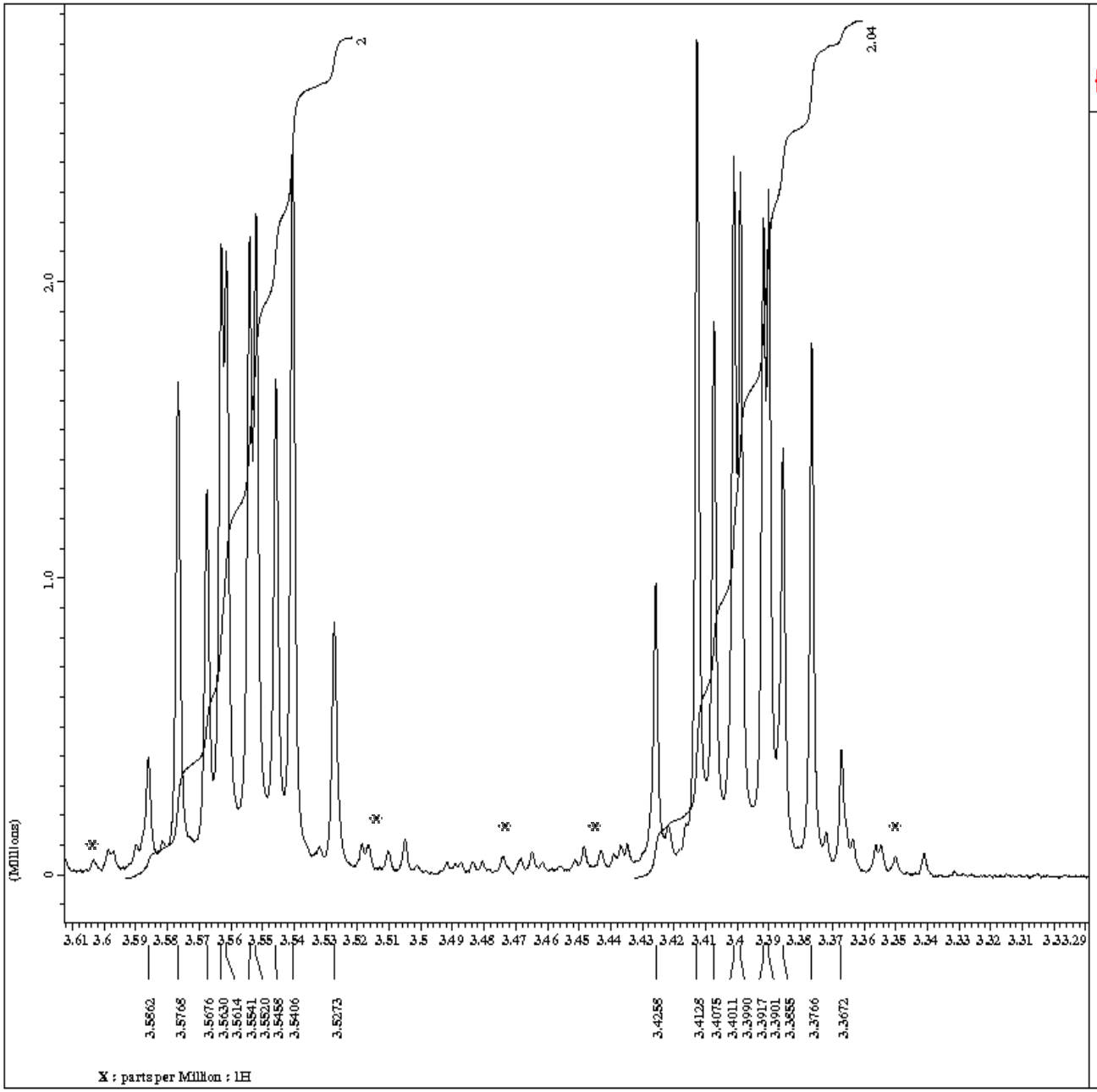
Comment           = Single Pulse Experime
Data_format       = 1D COMPLEX
Dim_size          = 65536
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

Field_strength    = 11.7473579[T]  (500[MH
X_acq_duration    = 0.7293952[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 5[ppm]
X_points          = 65536
X_prescans        = 0
X_resolution      = 0.11455547[Hz]
X_sweep           = 7.50750751[kHz]
Clipped           = FALSE
Mod_return        = 1
Scans             = 16
Total_scans       = 16

X_90_width        = 10.5[us]
X_acq_time        = 0.7293952[s]
X_angle           = 45[deg]
X_pulse           = 9.25[us]
Initial_wait      = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 24
Relaxation_delay  = 14[s]
Temp_get          = 25.1[dC]
Unblank_time      = 2[us]
```



143

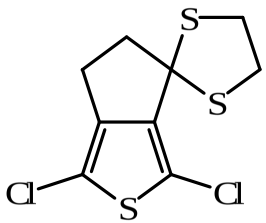


Filename = Dithilane -pent-cyc-t
Author = delta
Experiment = single_pulse.exp
Sample_id = S#457275
Solvent = CHLOROFORM-D
Creation_time = 1-FEB-2006 15:04:24
Revision_time = 4-NOV-2008 12:37:56
Current_time = 4-NOV-2008 12:38:58

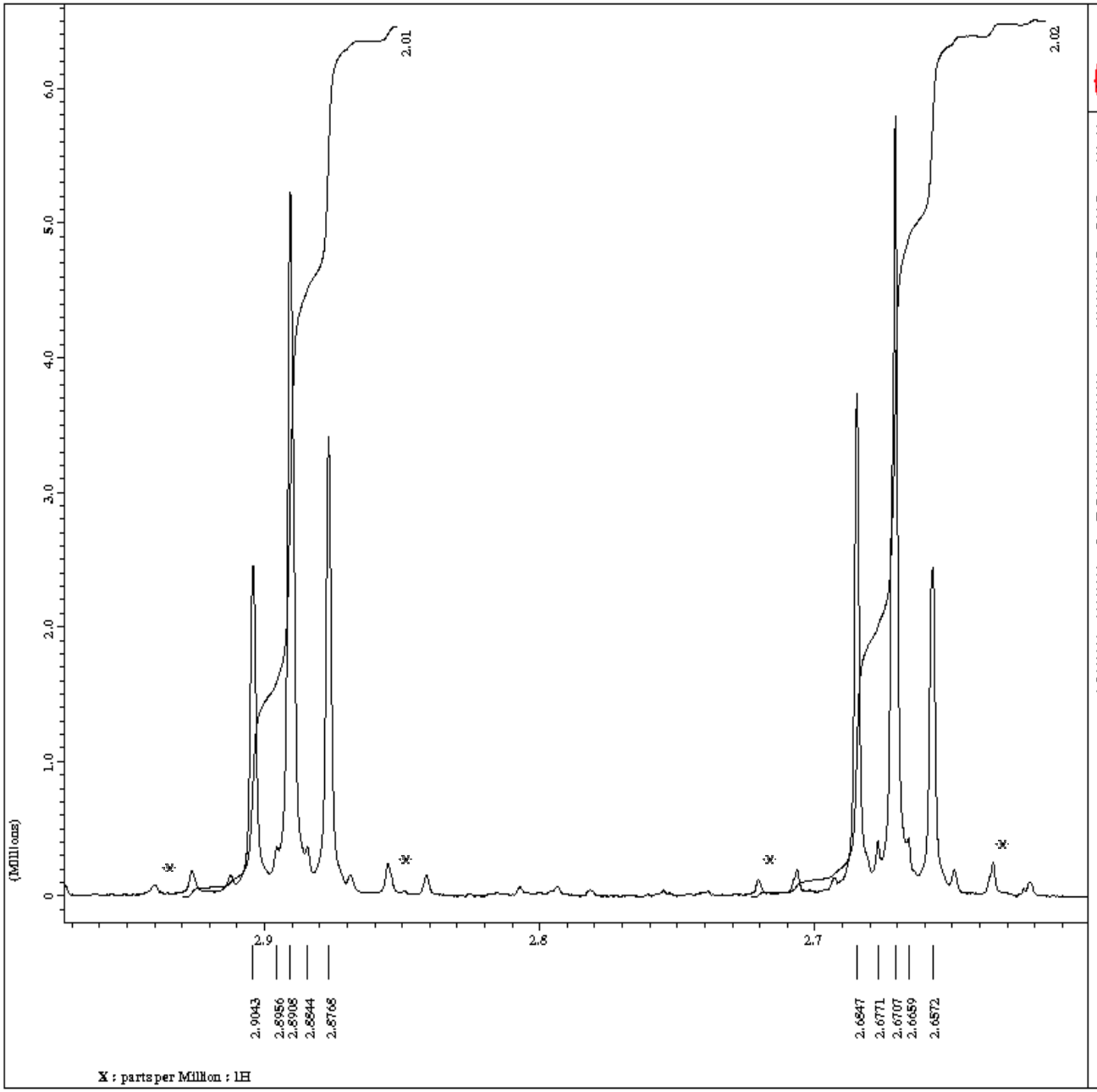
Comment = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 65536
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR

Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 0.7293952[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 65536
X_prescans = 0
X_resolution = 0.11455547[Hz]
X_sweep = 7.50750751[kHz]
Clipped = FALSE
Mod_return = 1
Scans = 16
Total_scans = 16

X_90_width = 10.5[us]
X_acq_time = 0.7293952[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 24
Relaxation_delay = 14[s]
Temp_get = 25.1[dC]
Unblank_time = 2[us]



143



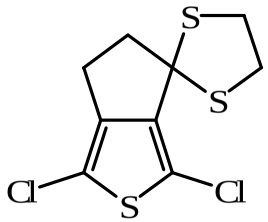
JEOL

```
Filename          = Dithilane -pent-cyc-t
Author            = delta
Experiment        = single_pulse.exp
Sample_id         = S#457275
Solvent           = CHLOROFORM-D
Creation_time     =  1-FEB-2006 15:04:24
Revision_time     =  4-NOV-2008 12:37:56
Current_time      =  4-NOV-2008 12:39:42

Comment           = Single Pulse Experime
Data_format       = 1D COMPLEX
Dim_size          = 65536
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 0.7293952[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 5[ppm]
X_points          = 65536
X_prescans        = 0
X_resolution      = 0.11455547[Hz]
X_sweep           = 7.50750751[kHz]
Clipped           = FALSE
Mod_return        = 1
Scans             = 16
Total_scans       = 16

X_90_width        = 10.5[us]
X_acq_time        = 0.7293952[s]
X_angle           = 45[deg]
X_pulse           = 9.25[us]
Initial_wait      = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 24
Relaxation_delay  = 14[s]
Temp_get          = 25.1[dC]
Unblank_time      = 2[us]
```



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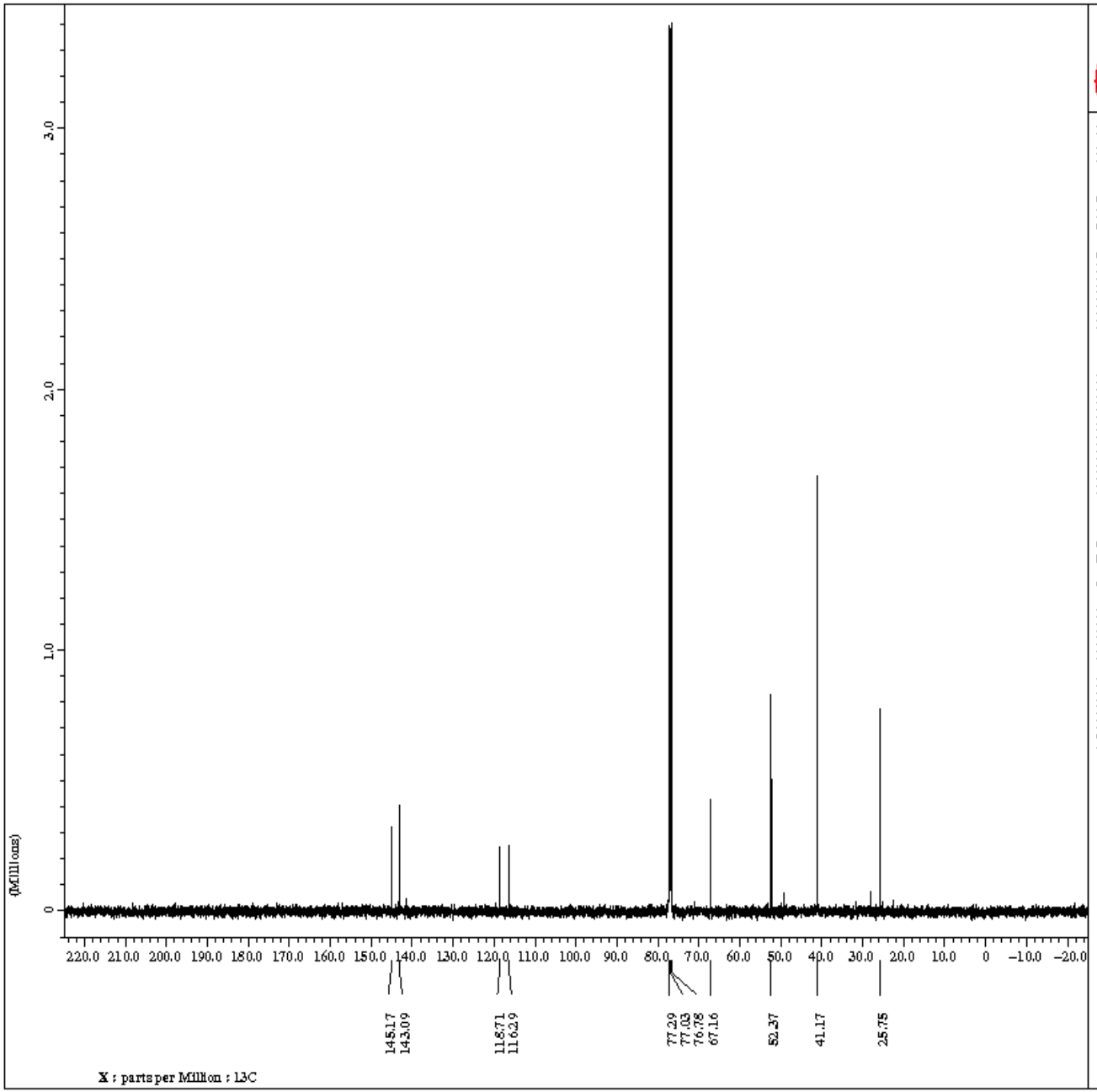


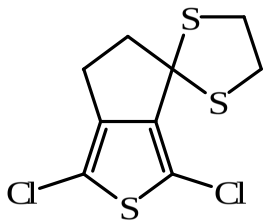
JEOL

```
Filename          = cp-dithiolane-3.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#752267
Solvent           = CHLOROFORM-D
Creation_time     = 13-NOV-2008 05:41:47
Revision_time     = 19-NOV-2008 11:31:02
Current_time      = 19-NOV-2008 11:32:52

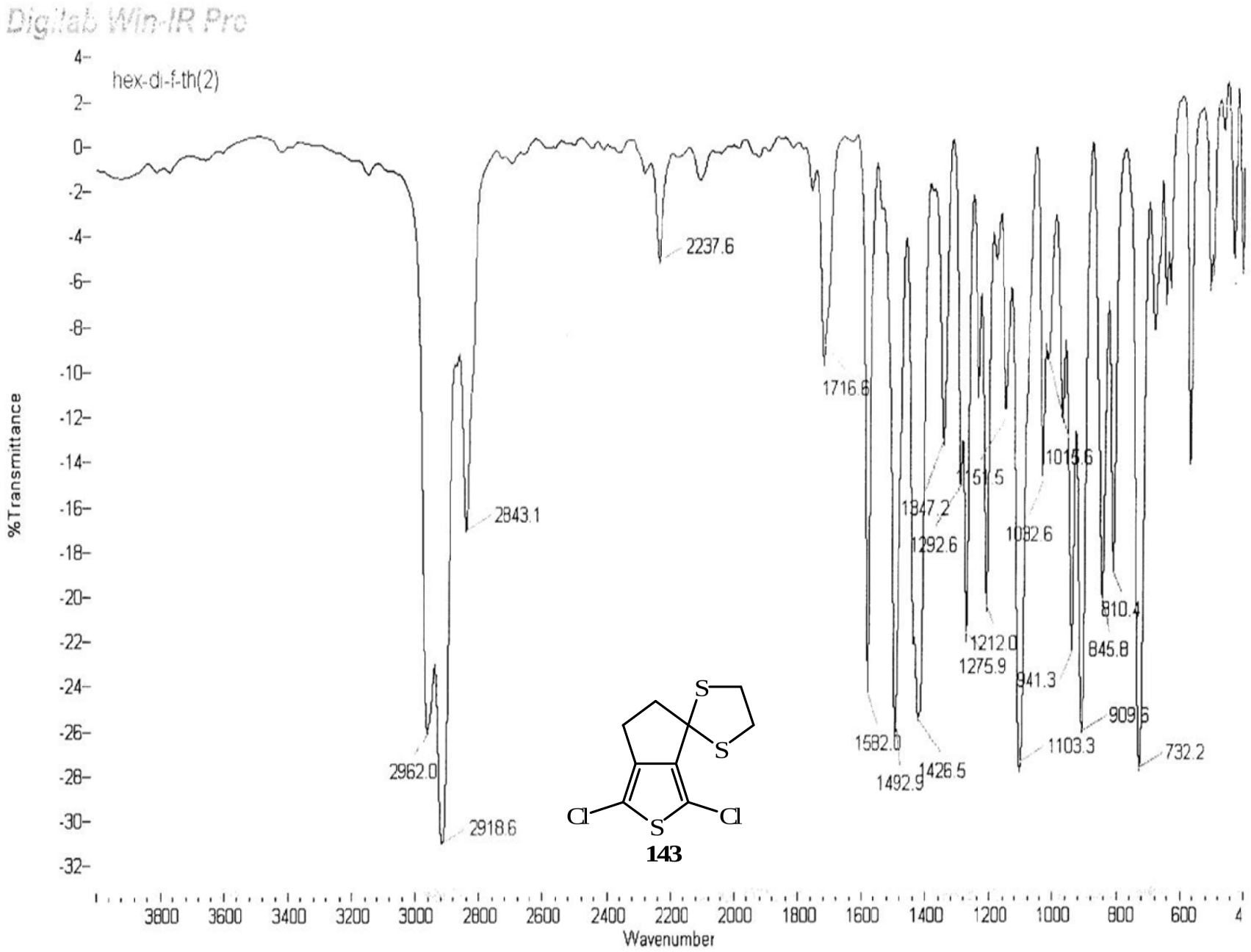
Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 65536
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 2.0840448[s]
X_domain          = 13C
X_freq            = 125.76529760[MHz]
X_offset          = 100[ppm]
X_points          = 65536
X_prescans        = 4
X_resolution      = 0.47983613[Hz]
X_sweep           = 31.44654088[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 723
Total_scans       = 723

X_90_width        = 14.2[us]
X_acq_time        = 2.0840448[s]
X_angle           = 30[deg]
X_pulse           = 4.73333333[us]
Initial_wait      = 1[s]
Noe_time          = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 30
Relaxation_delay  = 2[s]
Temp_get          = 20.6[dC]
Unblank_time      = 2[us]
```



143


Digilab Win-IR Pro
hex-di-f-th(2)
%Transmittance
Wavenumber
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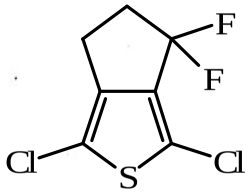
2918.6
2843.1
2237.6
1716.6
1582.0
1492.9
1426.5
1347.2
1292.6
1151.5
1212.0
1275.9
1082.6
1103.3
941.3
1015.6
845.8
810.4
909.6
732.2
Cl
Cl
S
S
S

143

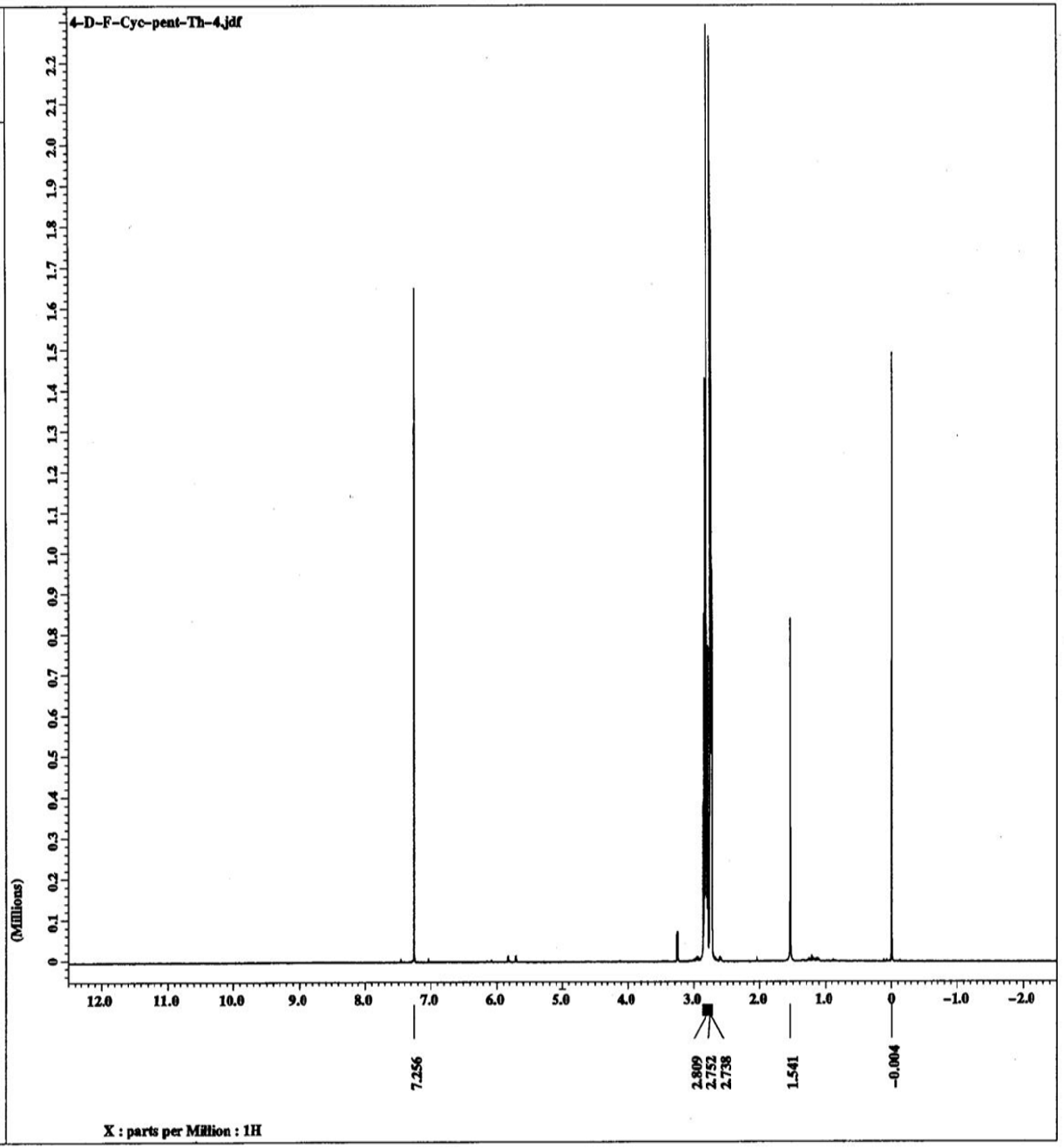
APPENDIX 21

^{1}H, ^{13}C, ^{19}F NMR and IR spectra of 1,3-dichloro-4,4-difluoro-5,6-dihydrocyclopenta[*c*]thiophene (**125**)

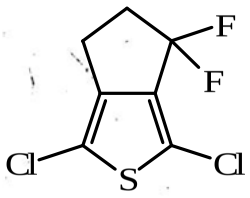
Filename	= 4-D-F-Cyc-pent-Th-4.j
Author	= delta
Experiment	= single_pulse.exp
Sample_id	= S0776602
Solvent	= CHLOROFORM-D
Creation_time	= 8-JUL-2006 22:25:45
Revision_time	= 8-JUL-2006 21:49:01
Current_time	= 8-JUL-2006 21:49:09
Content	= Single Pulse Experime
Data_format	= 1D COMPLEX
Dim_size	= 131072
Dim_title	= 1H
Dim_units	= [ppm]
Dimensions	= X
Site	= Eclipse+ 500
Spectrometer	= DELTA_NMR
Field_strength	= 11.7473579[T] (500[MH
X_acq_duration	= 17.4587904[s]
X_domain	= 1H
X_freq	= 500.15991521[MHz]
X_offset	= 5[ppm]
X_points	= 131072
X_prescans	= 0
X_resolution	= 57.27773672[mHz]
X_sweep	= 7.50750751[kHz]
Clipped	= FALSE
Mod_return	= 1
Scans	= 13
Total_scans	= 13
X_90_width	= 18.5[us]
X_acq_time	= 17.4587904[s]
X_angle	= 45[deg]
X_pulse	= 9.25[us]
Initial_wait	= 1[s]
Phase_preset	= 3[us]
Recvr_gain	= 21
Relaxation_delay	= 30[s]
Temp_get	= 25.3[dC]
Unblank_time	= 2[us]



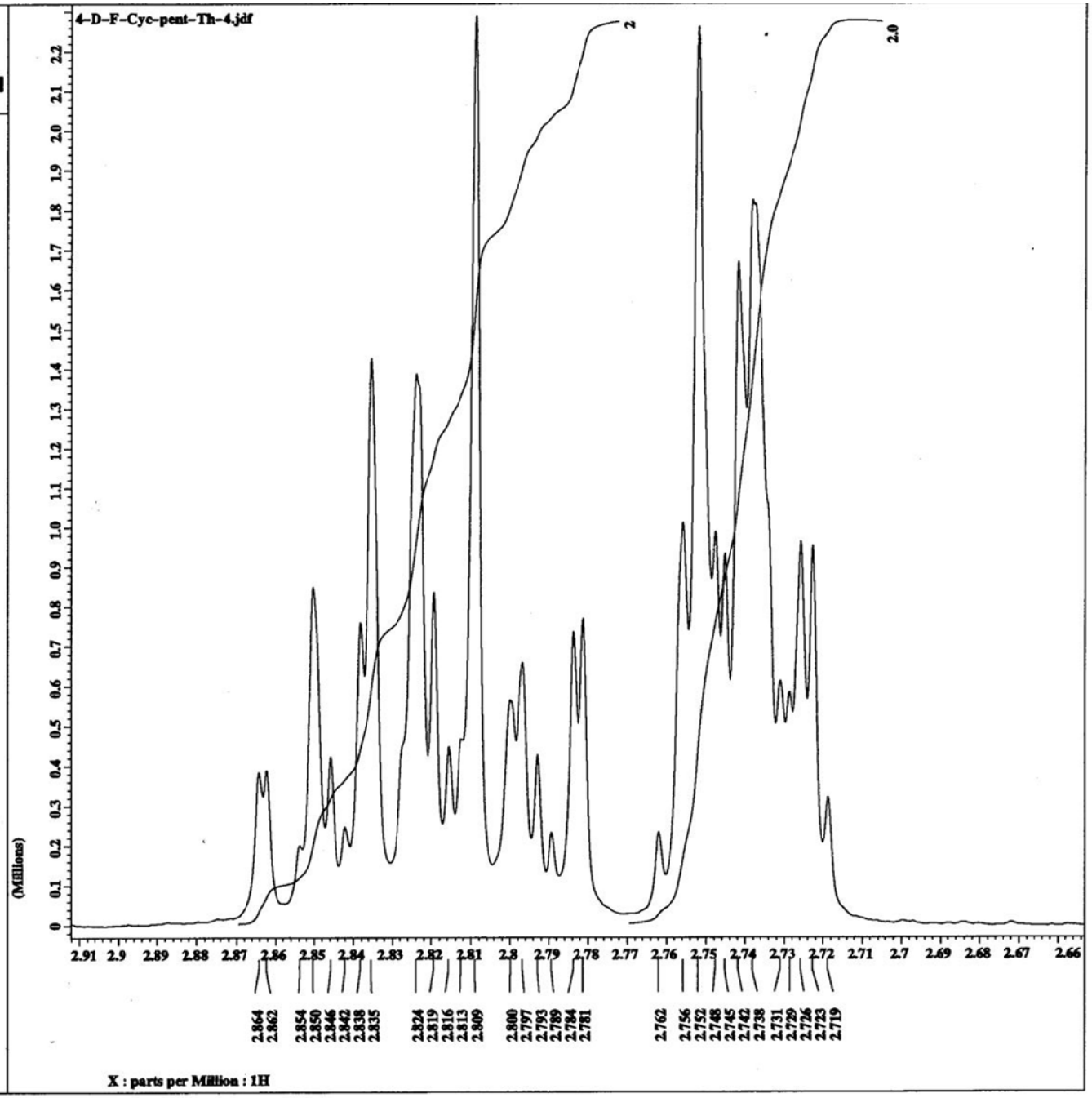
125



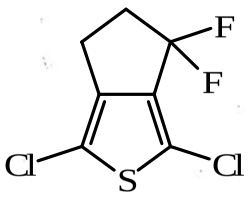
Filename	= 4-D-F-Cyc-pent-Th-4.j
Author	= delta
Experiment	= single_pulse.exp
Sample_id	= SS776602
Solvent	= CHLOROFORM-D
Creation_time	= 8-JUL-2006 22:25:45
Revision_time	= 8-JUL-2006 21:50:11
Current_time	= 8-JUL-2006 21:50:14
Content	= Single Pulse Experime
Data_format	= 1D COMPLEX
Dim_size	= 131072
Dim_title	= 1H
Dim_units	= [ppm]
Dimensions	= X
Site	= Eclipse+ 500
Spectrometer	= DELTA_NMR
Field_strength	= 11.7473579[T] (500[MH
X_acq_duration	= 17.4587904[s]
X_domain	= 1H
X_freq	= 500.15991521[MHz]
X_offset	= 5[ppm]
X_points	= 131072
X_prescans	= 0
X_resolution	= 57.27773672[mHz]
X_sweep	= 7.50750751[kHz]
Clipped	= FALSE
Mod_return	= 1
Scans	= 13
Total_scans	= 13
X_90_width	= 18.5[us]
X_acq_time	= 17.4587904[s]
X_angle	= 45[deg]
X_pulse	= 9.25[us]
Initial_wait	= 1[s]
Phase_preset	= 3[us]
Recvr_gain	= 21
Relaxation_delay	= 30[s]
Temp_get	= 25.3[dC]
Unblank_time	= 2[us]



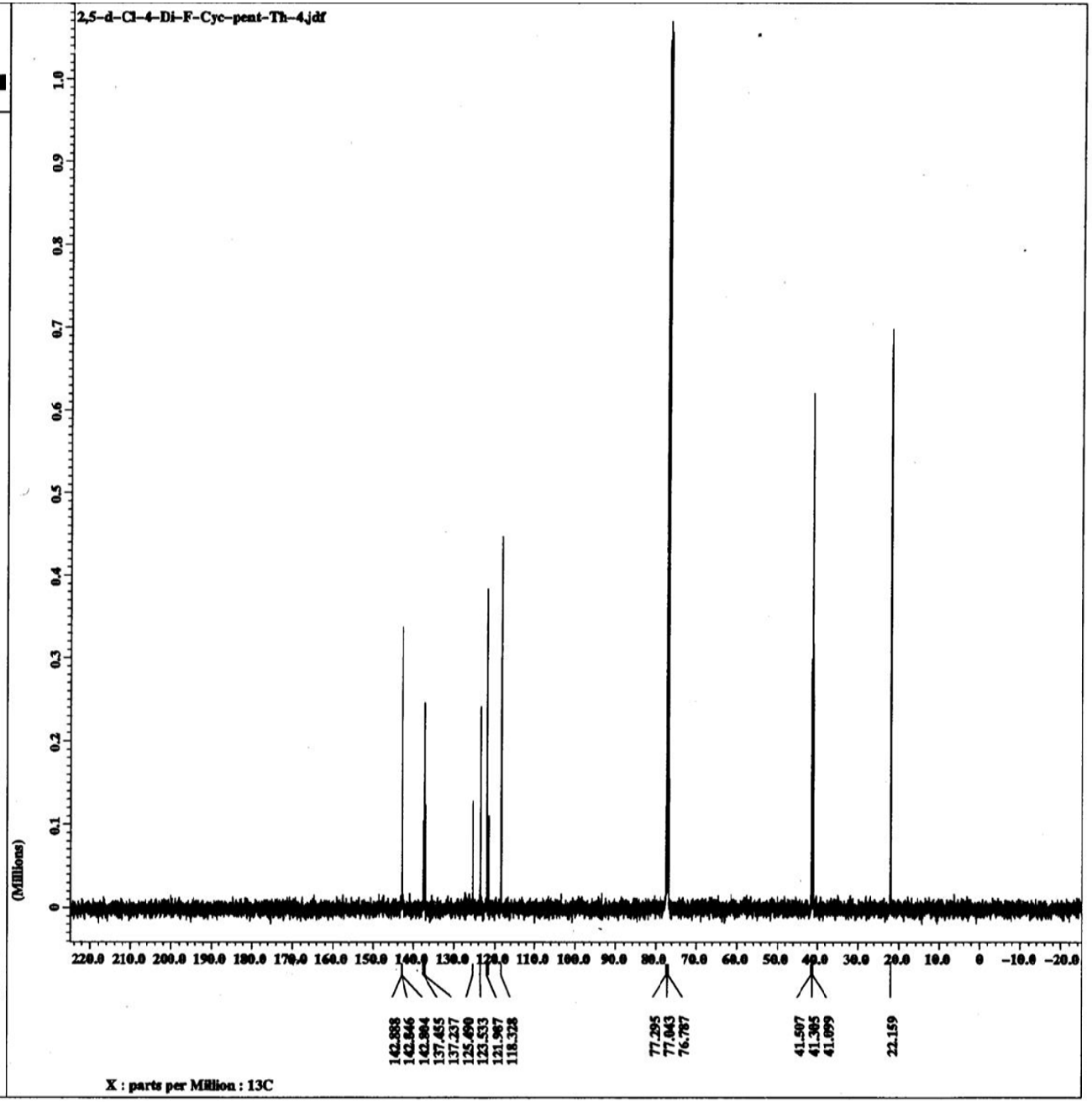
125



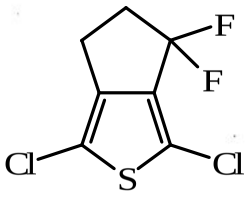
Filename	= 2,5-d-Cl-4-Di-F-Cyc-p
Author	= delta
Experiment	= single_pulse_dec
Sample_id	= #8713077
Solvent	= CHLOROFORM-D
Creation_time	= 9-JUL-2006 23:28:45
Revision_time	= 10-JUL-2006 23:12:01
Current_time	= 10-JUL-2006 23:12:03
Content	= Single Pulse with Bro
Data_format	= 1D COMPLEX
Dim_size	= 65536
Dim_title	= 13C
Dim_units	= [ppm]
Dimensions	= X
Site	= Eclipse+ 500
Spectrometer	= DELTA_NMR
Field_strength	= 11.7473579[T] (500[MH
X_acq_duration	= 2.0840448[s]
X_domain	= 13C
X_freq	= 125.76529768[MHz]
X_offset	= 100[ppm]
X_points	= 65536
X_prescans	= 4
X_resolution	= 0.47983613[Hz]
X_sweep	= 31.44654088[kHz]
Irr_domain	= 1H
Irr_freq	= 500.15991521[MHz]
Irr_offset	= 5[ppm]
Clipped	= FALSE
Mod_return	= 1
Scans	= 1500
Total_scans	= 1500
X_90_width	= 14.2[us]
X_acq_time	= 2.0840448[s]
X_angle	= 30[deg]
X_pulse	= 4.73333333[us]
Initial_wait	= 1[s]
Phase_preset	= 3[us]
Recvr_gain	= 30
Relaxation_delay	= 5[s]
Temp_get	= 28.2[dC]
Unblank_time	= 2[us]



125



Filename	= 2,5-d-Cl-4-Di-F-Cyc-p
Author	= delta
Experiment	= single_pulse_dec
Sample_id	= #713077
Solvent	= CHLOROFORM-D
Creation_time	= 9-JUL-2006 23:28:45
Revision_time	= 10-JUL-2006 23:12:01
Current_time	= 10-JUL-2006 23:13:58
Content	= Single Pulse with Bro
Data_format	= 1D COMPLEX
Dim_size	= 65536
Dim_title	= 13C
Dim_units	= [ppm]
Dimensions	= X
Site	= Eclipse+ 500
Spectrometer	= DELTA_NMR
Field_strength	= 11.7473579[T] (500[MH
X_acq_duration	= 2.0840448[s]
X_domain	= 13C
X_freq	= 125.76529768[MHz]
X_offset	= 100[ppm]
X_points	= 65536
X_prescans	= 4
X_resolution	= 0.47983613[Hz]
X_sweep	= 31.44654088[kHz]
Irr_domain	= 1H
Irr_freq	= 500.15991521[MHz]
Irr_offset	= 5[ppm]
Clipped	= FALSE
Mod_return	= 1
Scans	= 1500
Total_scans	= 1500
X_90_width	= 14.2[us]
X_acq_time	= 2.0840448[s]
X_angle	= 30[deg]
X_pulse	= 4.73333333[us]
Initial_wait	= 1[s]
Phase_preset	= 3[us]
Recvr_gain	= 30
Relaxation_delay	= 5[s]
Temp_get	= 28.2[dC]
Unblank_time	= 2[us]



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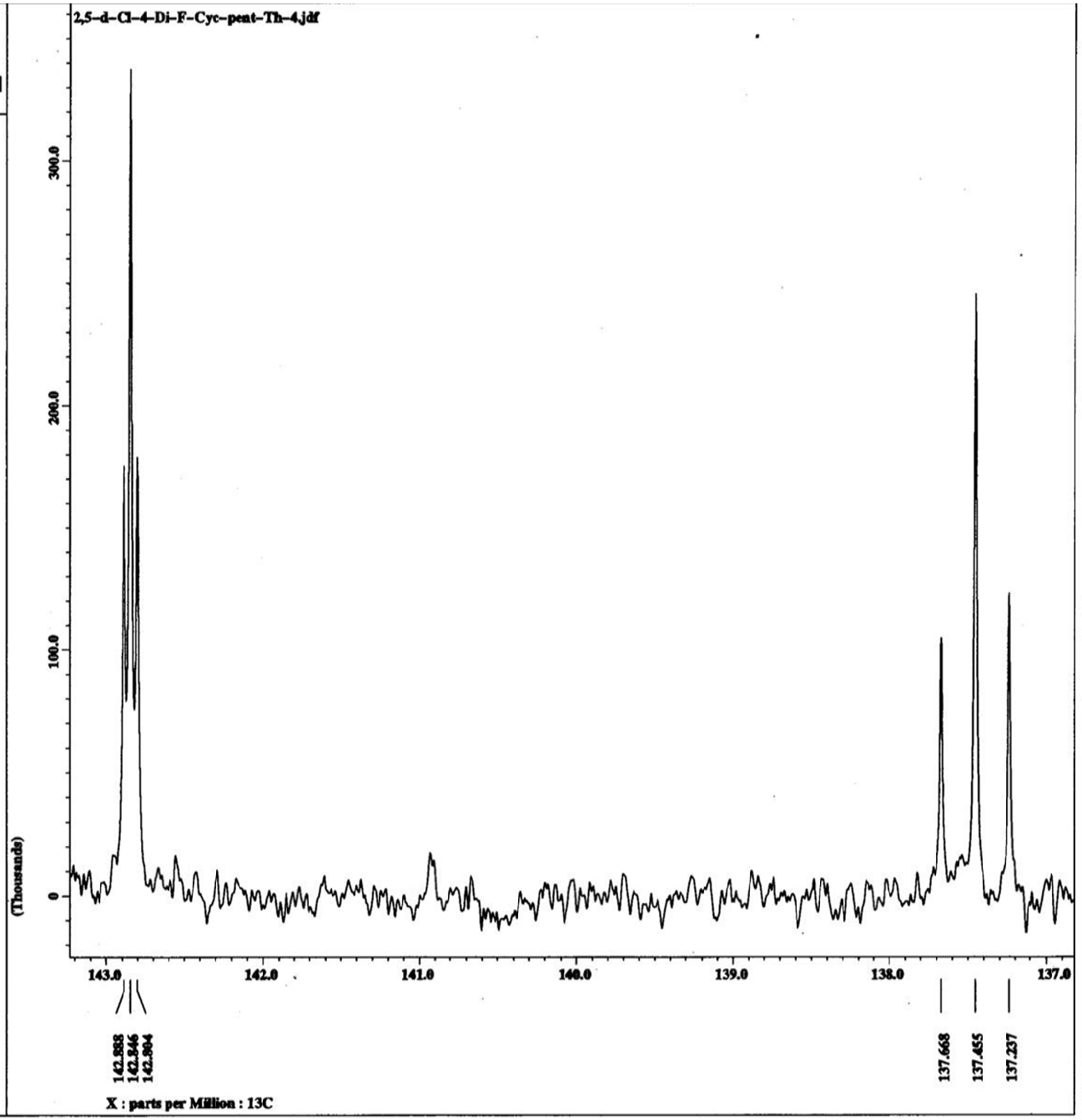
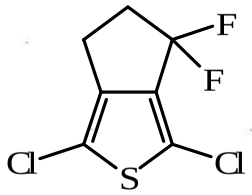


JEOL

Filename	= 2,5-d-Cl-4-Di-F-Cyc-p
Author	= delta
Experiment	= single_pulse_dec
Sample_id	= #0713077
Solvent	= CHLOROFORM-D
Creation_time	= 9-JUL-2006 23:28:45
Revision_time	= 10-JUL-2006 23:12:01
Current_time	= 10-JUL-2006 23:13:37
Content	= Single Pulse with Bro
Data_format	= 1D COMPLEX
Dim_size	= 65536
Dim_title	= 13C
Dim_units	= [ppm]
Dimensions	= X
Site	= Eclipse+ 500
Spectrometer	= DELTA_NMR
Field_strength	= 11.7473579[T] (500[MH
X_acq_duration	= 2.0840448[s]
X_domain	= 13C
X_freq	= 125.76529768[MHz]
X_offset	= 100[ppm]
X_points	= 65536
X_prescans	= 4
X_resolution	= 0.47983613[Hz]
X_sweep	= 31.44654088[kHz]
Irr_domain	= 1H
Irr_freq	= 500.15991521[MHz]
Irr_offset	= 5[ppm]
Clipped	= FALSE
Mod_return	= 1
Scans	= 1500
Total_scans	= 1500
X_90_width	= 14.2[us]
X_acq_time	= 2.0840448[s]
X_angle	= 30[deg]
X_pulse	= 4.73333333[us]
Initial_wait	= 1[s]
Phase_preset	= 3[us]
Recvr_gain	= 30
Relaxation_delay	= 5[s]
Temp_get	= 28.2[dC]
Unblank_time	= 2[us]



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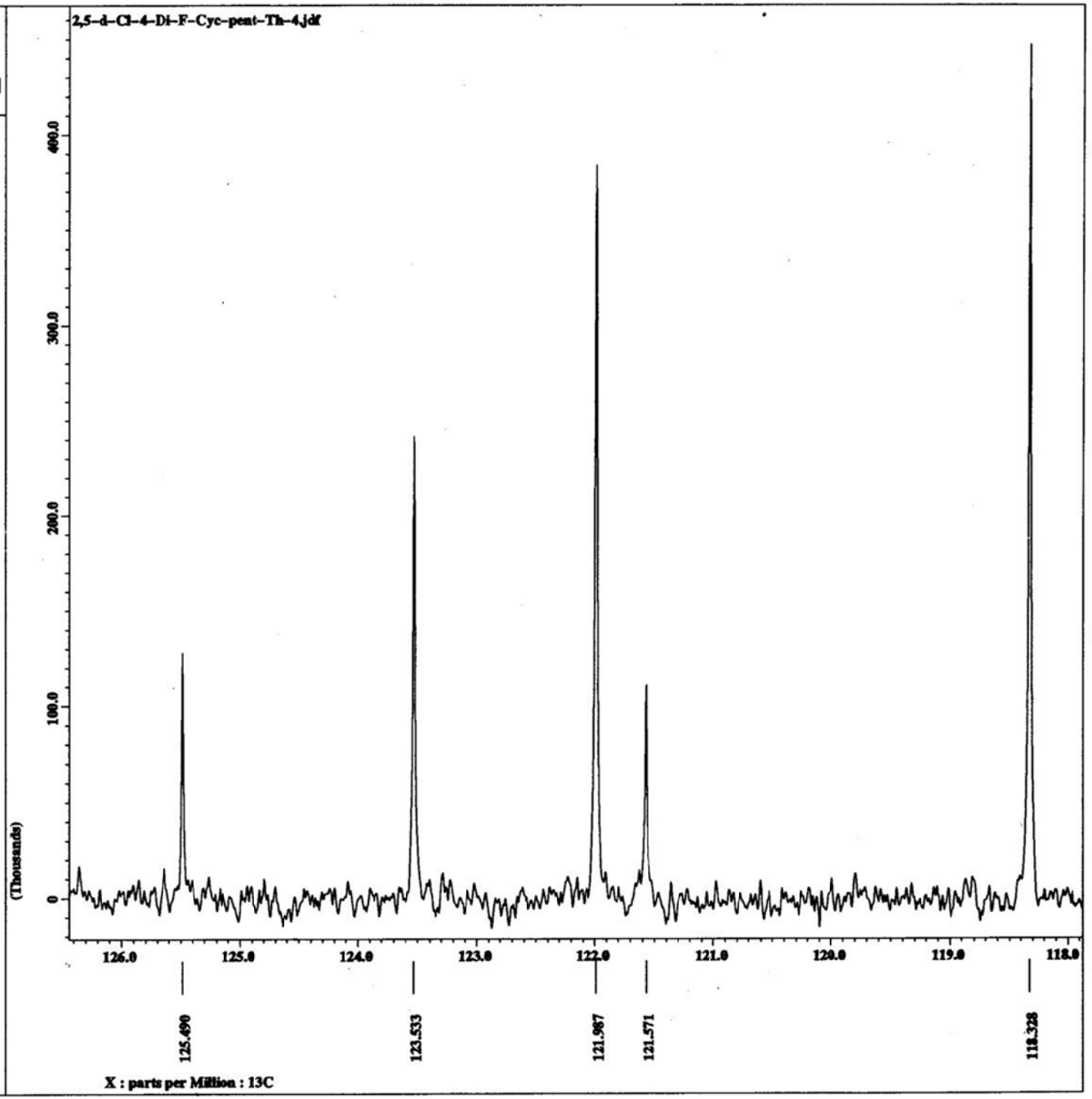
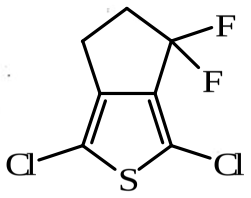
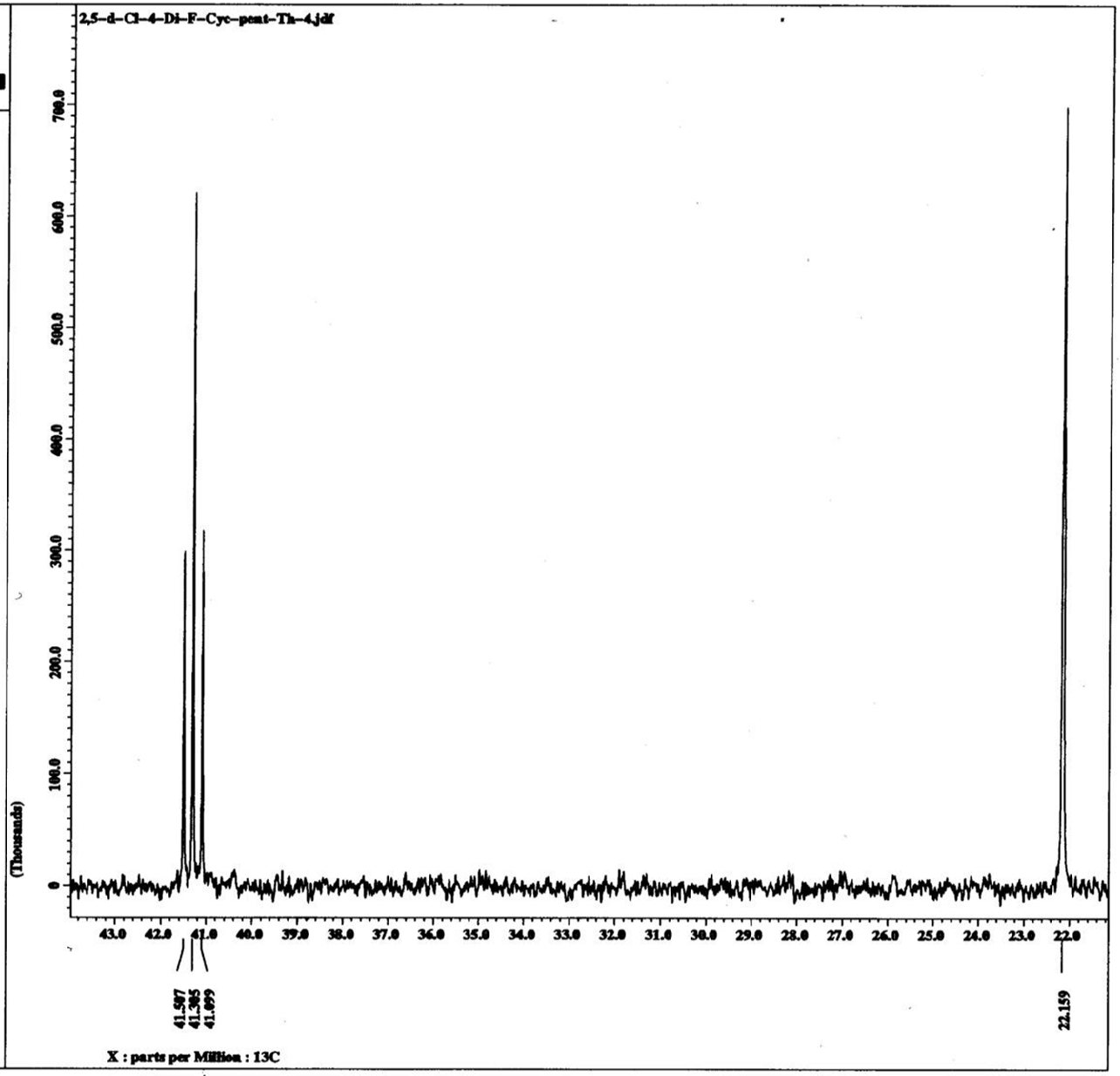


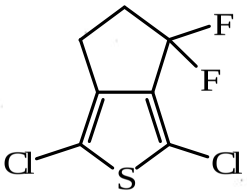
Filename	= 2,5-d-Cl-4-Di-F-Cyc-p
Author	= delta
Experiment	= single_pulse_dec
Sample_id	= s8713077
Solvent	= CHLOROFORM-D
Creation_time	= 9-JUL-2006 23:28:45
Revision_time	= 10-JUL-2006 23:12:01
Current_time	= 10-JUL-2006 23:13:05
Content	= Single Pulse with Bro
Data_format	= 1D COMPLEX
Dim_size	= 65536
Dim_title	= 13C
Dim_units	= [ppm]
Dimensions	= X
Site	= Eclipse+ 500
Spectrometer	= DELTA_NMR
Field_strength	= 11.7473579[T] (500[MH
X_acq_duration	= 2.0840448[s]
X_domain	= 13C
X_freq	= 125.76529768[MHz]
X_offset	= 100[ppm]
X_points	= 65536
X_prescans	= 4
X_resolution	= 0.47983613[Hz]
X_sweep	= 31.44654088[kHz]
Irr_domain	= 1H
Irr_freq	= 500.15991521[MHz]
Irr_offset	= 5[ppm]
Clipped	= FALSE
Mod_return	= 1
Scans	= 1500
Total_scans	= 1500
X_90_width	= 14.2[us]
X_acq_time	= 2.0840448[s]
X_angle	= 30[deg]
X_pulse	= 4.73333333[us]
Initial_wait	= 1[s]
Phase_preset	= 3[us]
Recvr_gain	= 30
Relaxation_delay	= 5[s]
Temp_get	= 28.2[dC]
Unblank_time	= 2[us]



125



Filename	= 2,5-Di-Cl-di-F-cyc.pe
Author	= delta
Experiment	= single_pulse.exp
Sample_id	= s07290824
Solvent	= CHLOROFORM-D
Creation_time	= 11-JUL-2006 21:12:12
Revision_time	= 11-JUL-2006 20:38:03
Current_time	= 11-JUL-2006 20:38:12
Content	= Single Pulse Experime
Data_format	= 1D COMPLEX
Dim_size	= 131072
Dim_title	= 19F
Dim_units	= [ppm]
Dimensions	= X
Site	= Eclipse+ 500
Spectrometer	= DELTA_NMR
Field_strength	= 11.7473579[T] (500[MH
X_acq_duration	= 1.7301504[s]
X_domain	= 19F
X_freq	= 470.62046084[MHz]
X_offset	= -60[ppm]
X_points	= 131072
X_prescans	= 0
X_resolution	= 0.57798443[Hz]
X_sweep	= 75.75757576[kHz]
Clipped	= FALSE
Mod_return	= 1
Scans	= 25
Total_scans	= 25
X_90_width	= 16[us]
X_acq_time	= 1.7301504[s]
X_angle	= 45[deg]
X_pulse	= 8[us]
Initial_wait	= 1[s]
Phase_preset	= 3[us]
Recvr_gain	= 17
Relaxation_delay	= 20[s]
Temp_get	= 25.7[dC]
Unblank_time	= 2[us]



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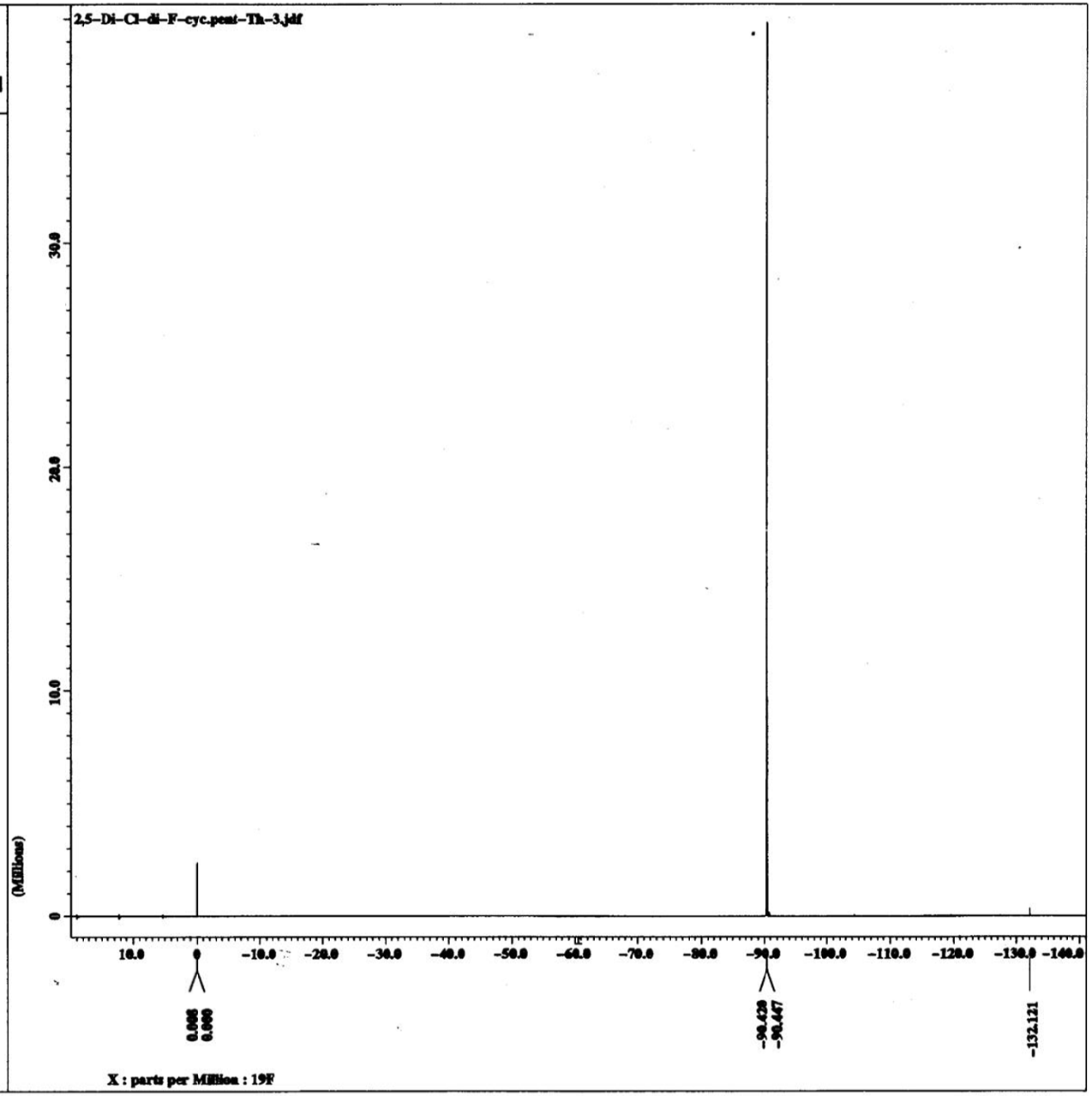
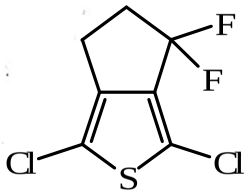
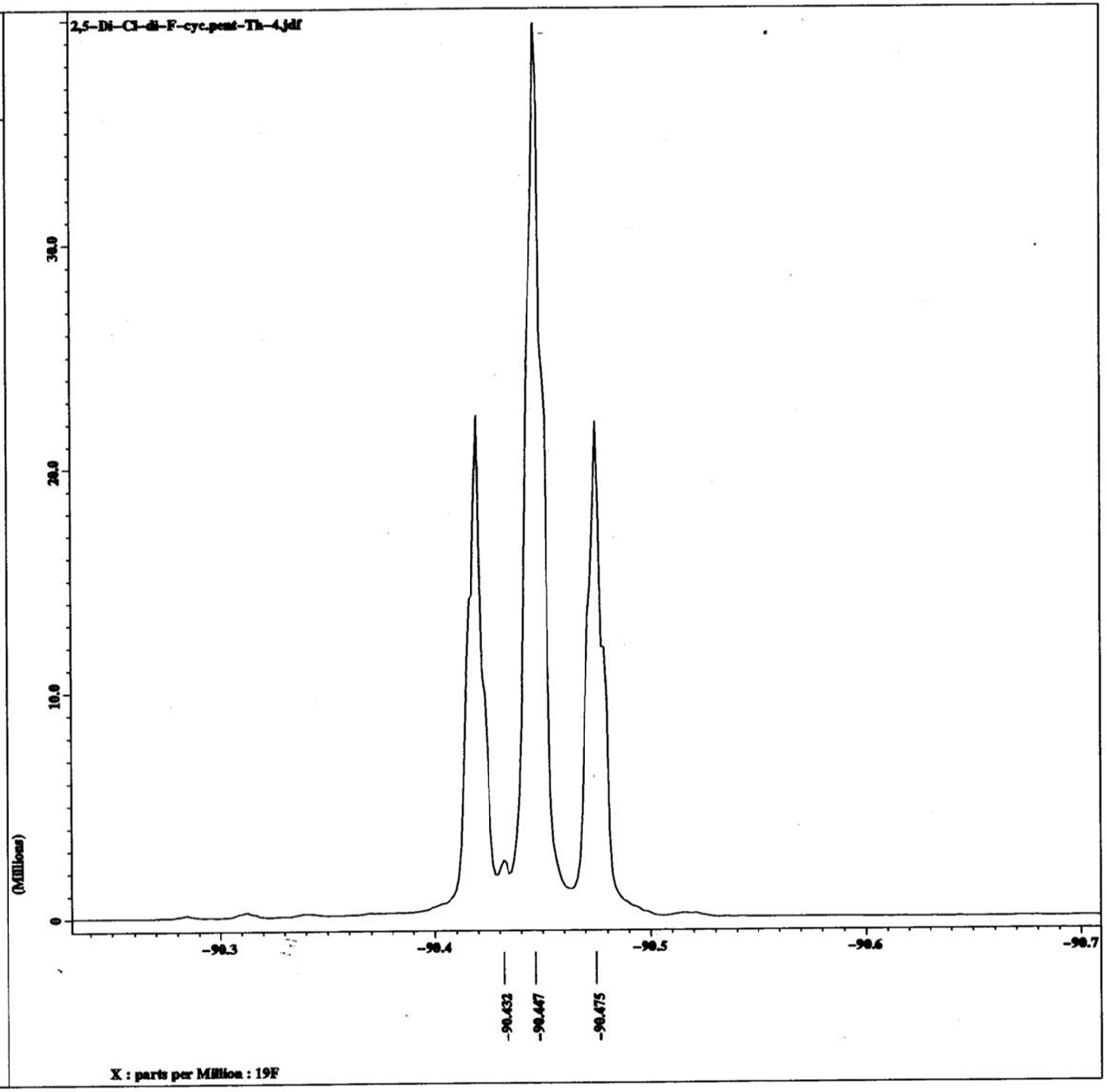
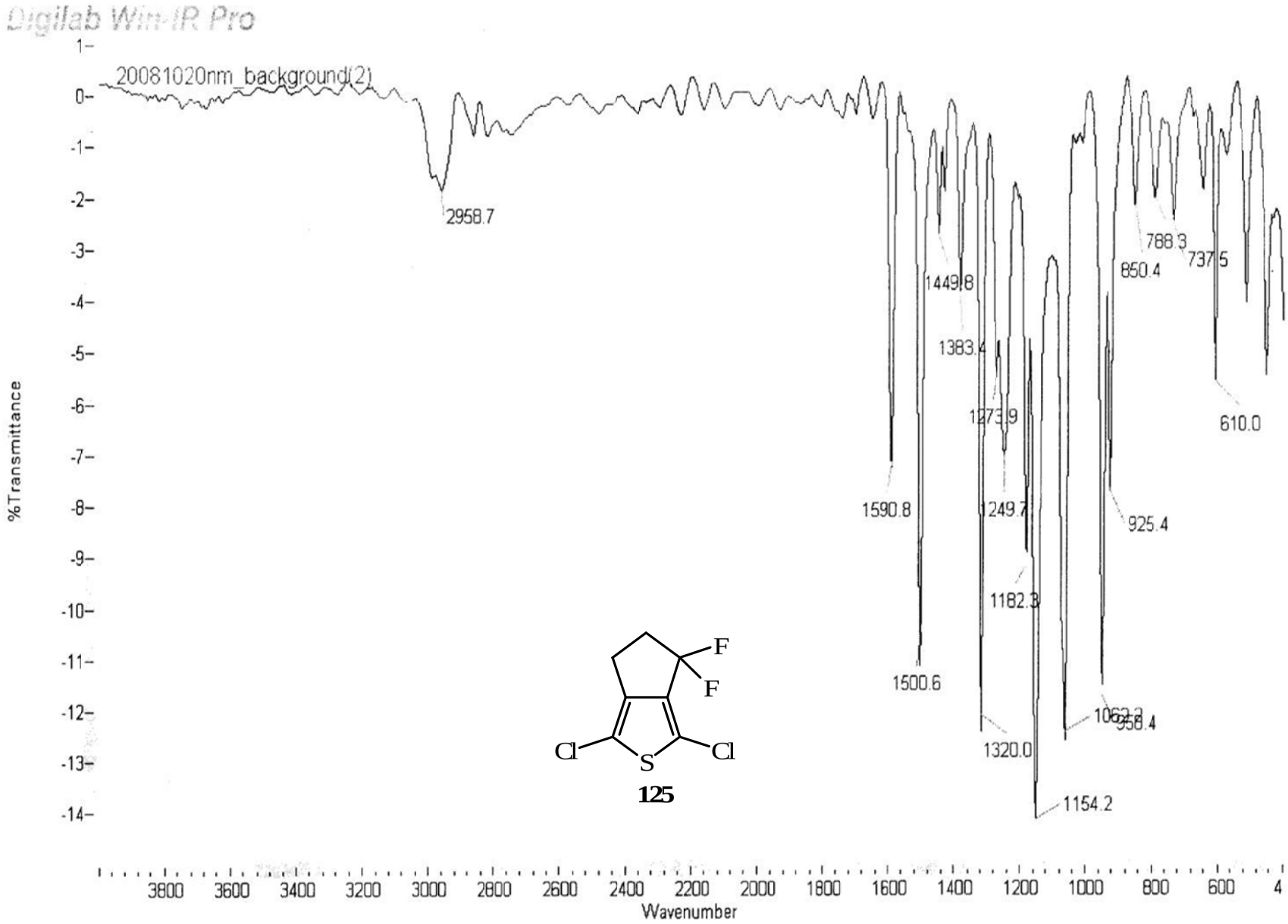


Filename	= 2,5-Di-Cl-di-F-cyc.pe
Author	= delta
Experiment	= single_pulse.exp
Sample_id	= 80729824
Solvent	= CHLOROFORM-D
Creation_time	= 11-JUL-2006 21:12:12
Revision_time	= 11-JUL-2006 20:39:13
Current_time	= 11-JUL-2006 20:39:24
Content	= Single Pulse Experime
Data_format	= 1D COMPLEX
Dim_size	= 131072
Dim_title	= 19F
Dim_units	= [ppm]
Dimensions	= X
Site	= Eclipse+ 500
Spectrometer	= DELTA_NMR
Field_strength	= 11.7473579[T] (500[MH
X_acq_duration	= 1.7301504[s]
X_domain	= 19F
X_freq	= 470.62046084[MHz]
X_offset	= -60[ppm]
X_points	= 131072
X_prescans	= 0
X_resolution	= 0.57798443[Hz]
X_sweep	= 75.75757576[kHz]
Clipped	= FALSE
Mod_return	= 1
Scans	= 25
Total_scans	= 25
X_90_width	= 16[us]
X_acq_time	= 1.7301504[s]
X_angle	= 45[deg]
X_pulse	= 8[us]
Initial_wait	= 1[s]
Phase_preset	= 3[us]
Recvr_gain	= 17
Relaxation_delay	= 20[s]
Temp_get	= 25.7[dC]
Unblank_time	= 2[us]



125

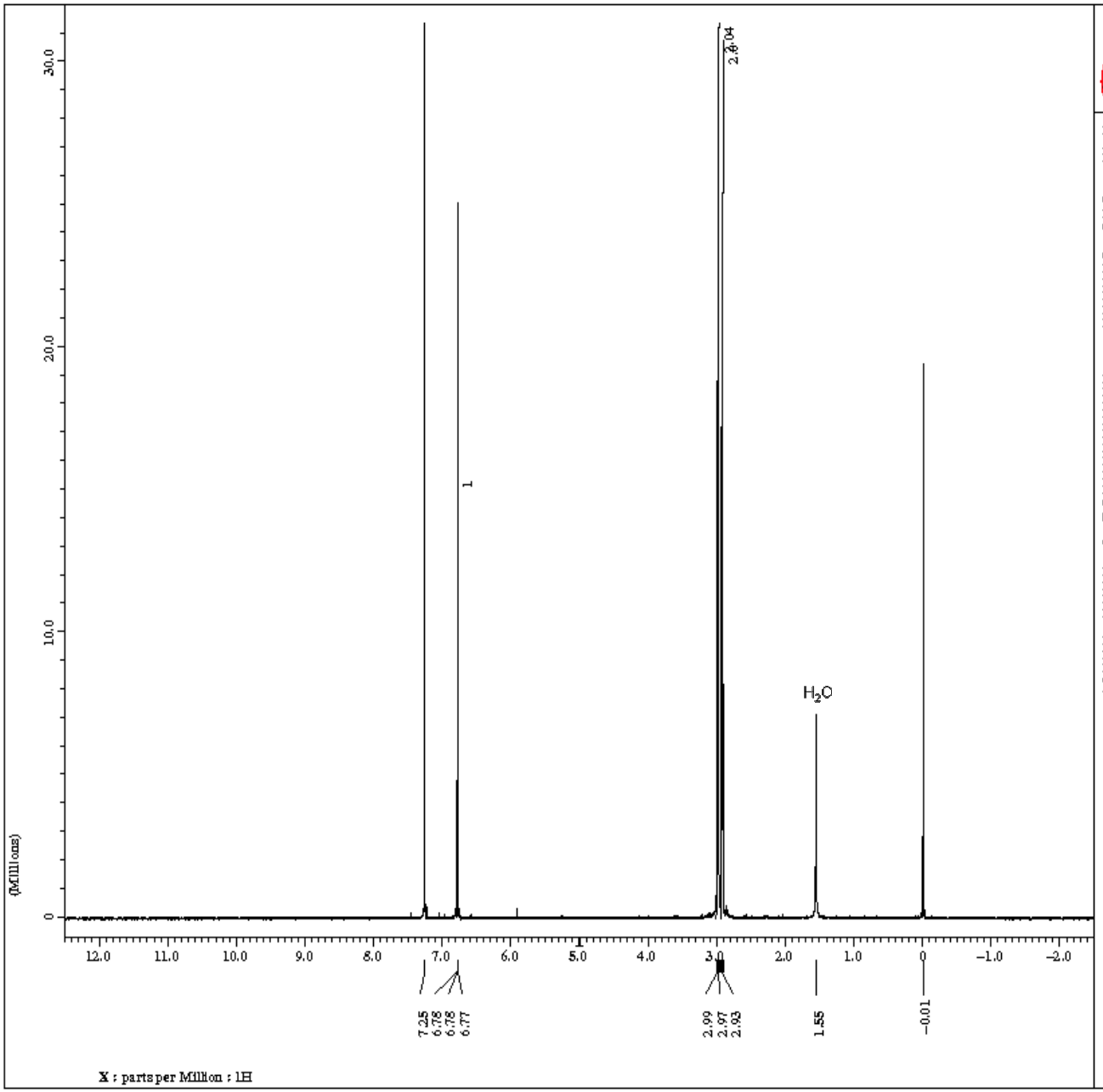



Digilab Win-IR Pro
20081020nm_background(2)
%Transmittance
Wavenumber
2958.7
1590.8
1500.6
1449.8
1383.4
1320.0
1273.9
1249.7
1182.3
1154.2
1062.2
958.4
925.4
850.4
788.3
737.5
610.0
F
F
Cl
Cl
S

125

APPENDIX 22

^{1}H, ^{13}C NMR and IR spectra of 3-chloro-5,6-dihidrorocyclopenta[*c*]thiophen-4-one (**144**)



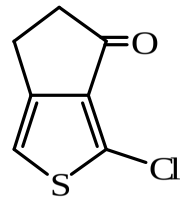
JEOL

```
Filename          = 3-Cl-th-cp-5.jdf
Author            = delta
Experiment        = single_pulse.exp
Sample_id         = S#727015
Solvent           = CHLOROFORM-D
Creation_time     = 11-NOV-2008 02:58:57
Revision_time     = 17-NOV-2008 13:18:10
Current_time      = 17-NOV-2008 13:18:25

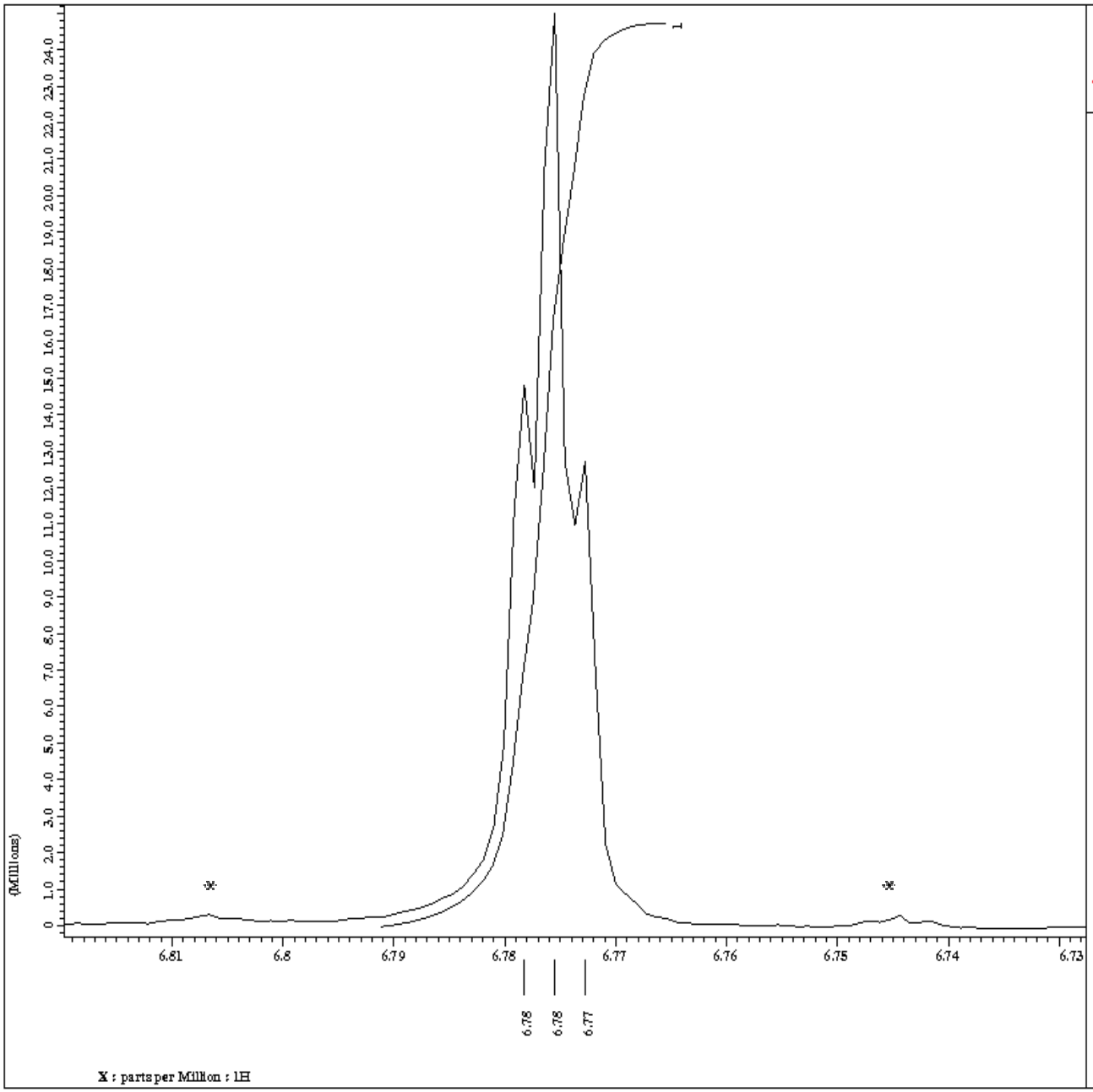
Comment           = Single Pulse Experime
Data_format       = 1D COMPLEX
Dim_size          = 16384
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 2.1823488[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 5[ppm]
X_points          = 16384
X_prescans        = 0
X_resolution      = 0.45822189[Hz]
X_sweep           = 7.50750751[kHz]
Clipped           = FALSE
Mod_return        = 1
Scans             = 8
Total_scans       = 8

X_90_width        = 10.5[us]
X_acq_time        = 2.1823488[s]
X_angle           = 45[deg]
X_pulse           = 9.25[us]
Initial_wait      = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 25
Relaxation_delay  = 14[s]
Temp_get          = 25.9[dC]
Unblank_time      = 2[us]
```



144



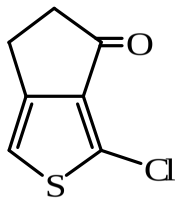
JEOL

```
Filename          = 3-Cl-th-cp-5.jdf
Author            = delta
Experiment        = single_pulse.exp
Sample_id         = S#727015
Solvent           = CHLOROFORM-D
Creation_time     = 11-NOV-2008 02:58:57
Revision_time     = 17-NOV-2008 13:18:10
Current_time      = 17-NOV-2008 13:21:15

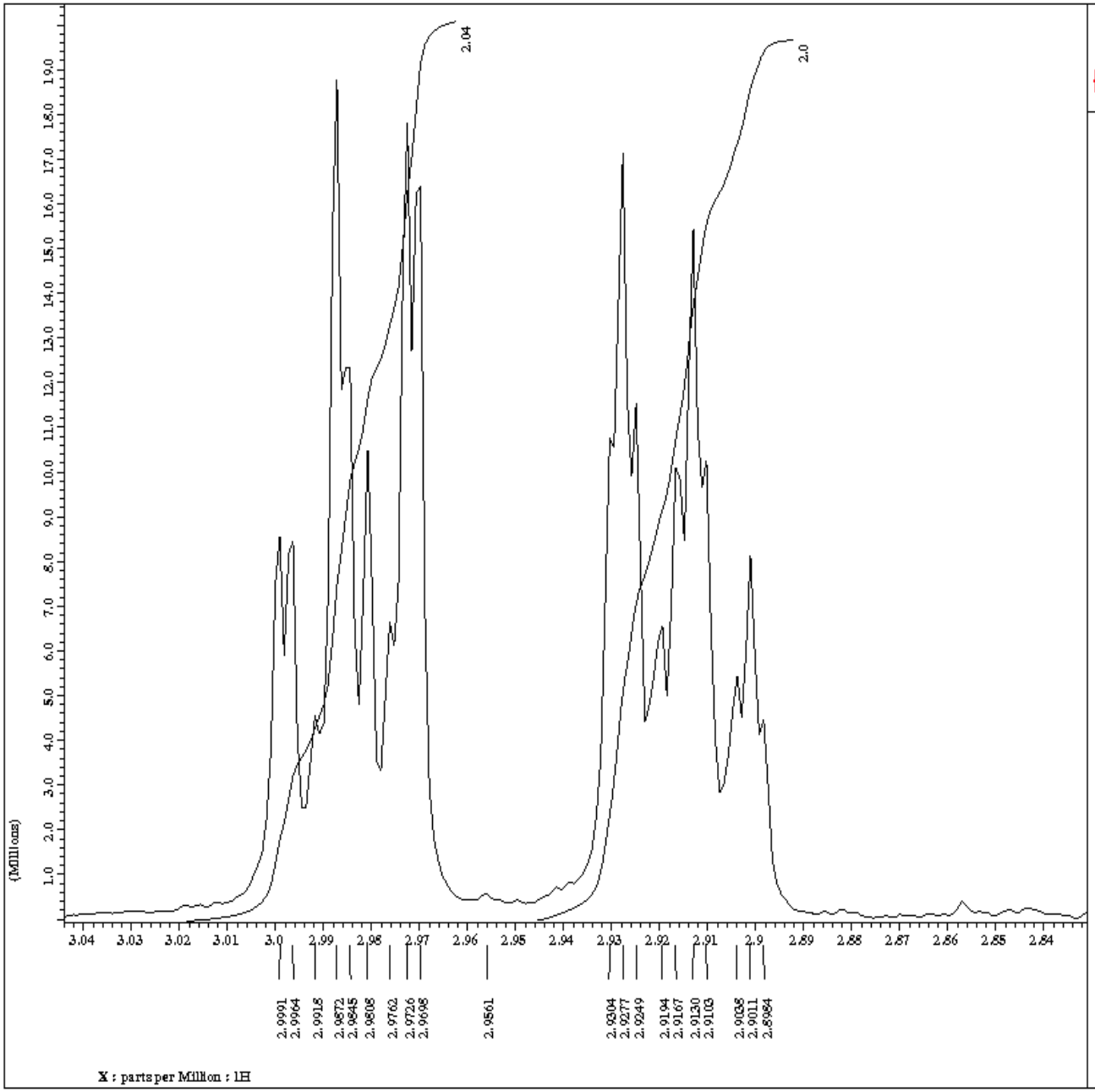
Comment           = Single Pulse Experime
Data_format       = 1D COMPLEX
Dim_size          = 16384
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 2.1023488[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 5[ppm]
X_points          = 16384
X_prescans        = 0
X_resolution      = 0.45822189[Hz]
X_sweep           = 7.50750751[kHz]
Clipped           = FALSE
Mod_return        = 1
Scans             = 8
Total_scans       = 8

X_90_width        = 10.5[us]
X_acq_time        = 2.1023488[s]
X_angle           = 45[deg]
X_pulse           = 9.25[us]
Initial_wait      = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 25
Relaxation_delay  = 14[s]
Temp_get          = 25.9[dC]
Unblank_time      = 2[us]
```



144



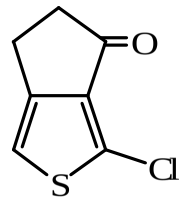
JEOL

```
Filename          = 3-Cl-th-cp-5.jdf
Author            = delta
Experiment        = single_pulse.exp
Sample_id         = S#727015
Solvent           = CHLOROFORM-D
Creation_time     = 11-NOV-2008 02:58:57
Revision_time     = 13-NOV-2008 14:36:16
Current_time      = 13-NOV-2008 14:47:32

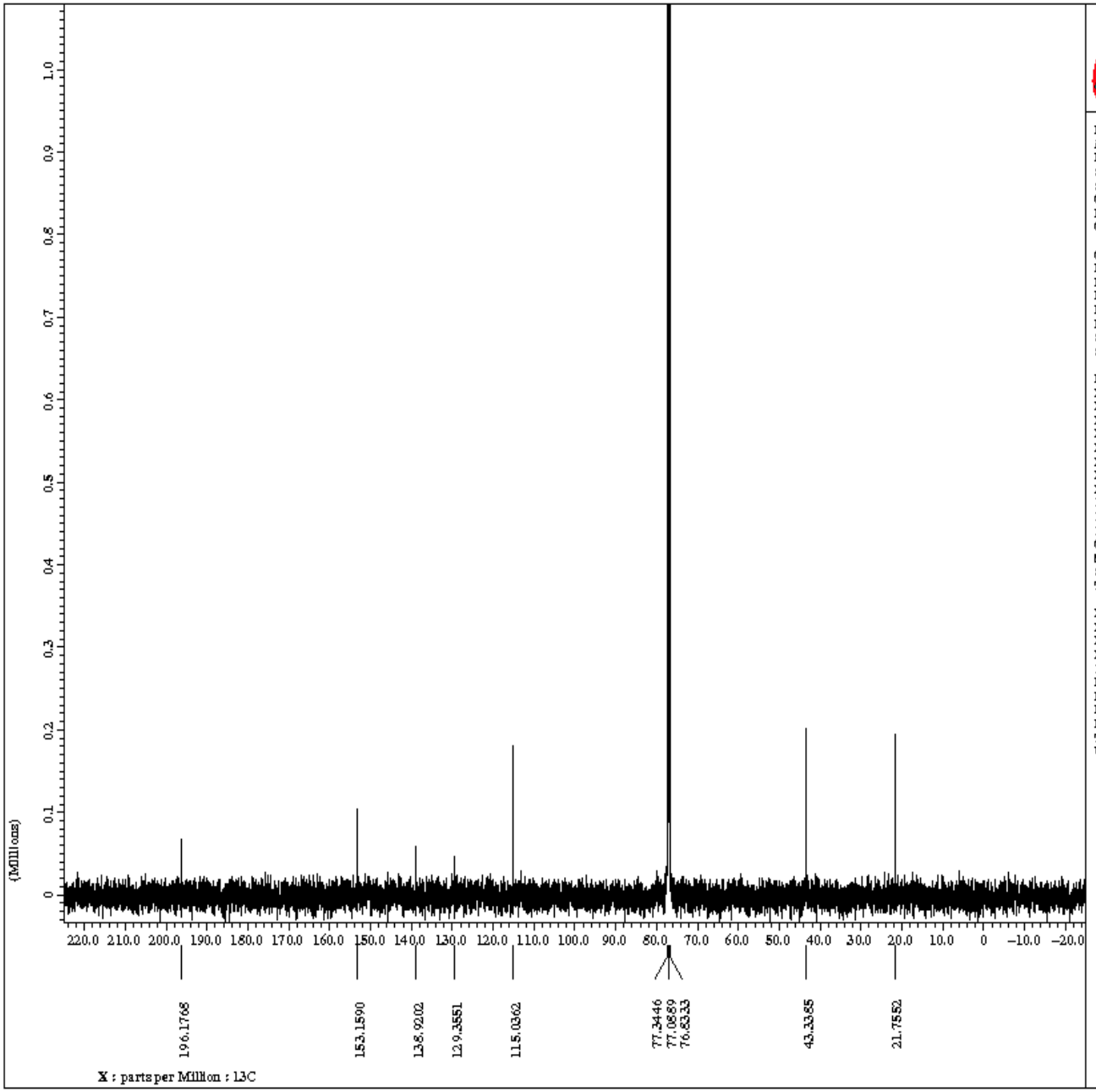
Comment           = Single Pulse Experime
Data_format       = 1D COMPLEX
Dim_size          = 16384
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 2.1023488[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 5[ppm]
X_points          = 16384
X_prescans        = 0
X_resolution      = 0.45822189[Hz]
X_sweep           = 7.50750751[kHz]
Clipped           = FALSE
Mod_return        = 1
Scans             = 8
Total_scans       = 8

X_90_width        = 18.5[us]
X_acq_time        = 2.1023488[s]
X_angle           = 45[deg]
X_pulse           = 9.25[us]
Initial_wait      = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 25
Relaxation_delay  = 14[s]
Temp_get          = 25.9[dC]
Unblank_time      = 2[us]
```



144



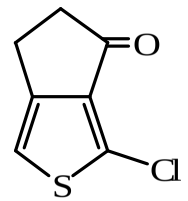
JEOL

Filename = 3-Cl-th-cp-3.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = S#729848
Solvent = CHLOROFORM-D
Creation_time = 11-NOV-2008 04:07:22
Revision_time = 11-NOV-2008 20:14:19
Current_time = 11-NOV-2008 20:15:30

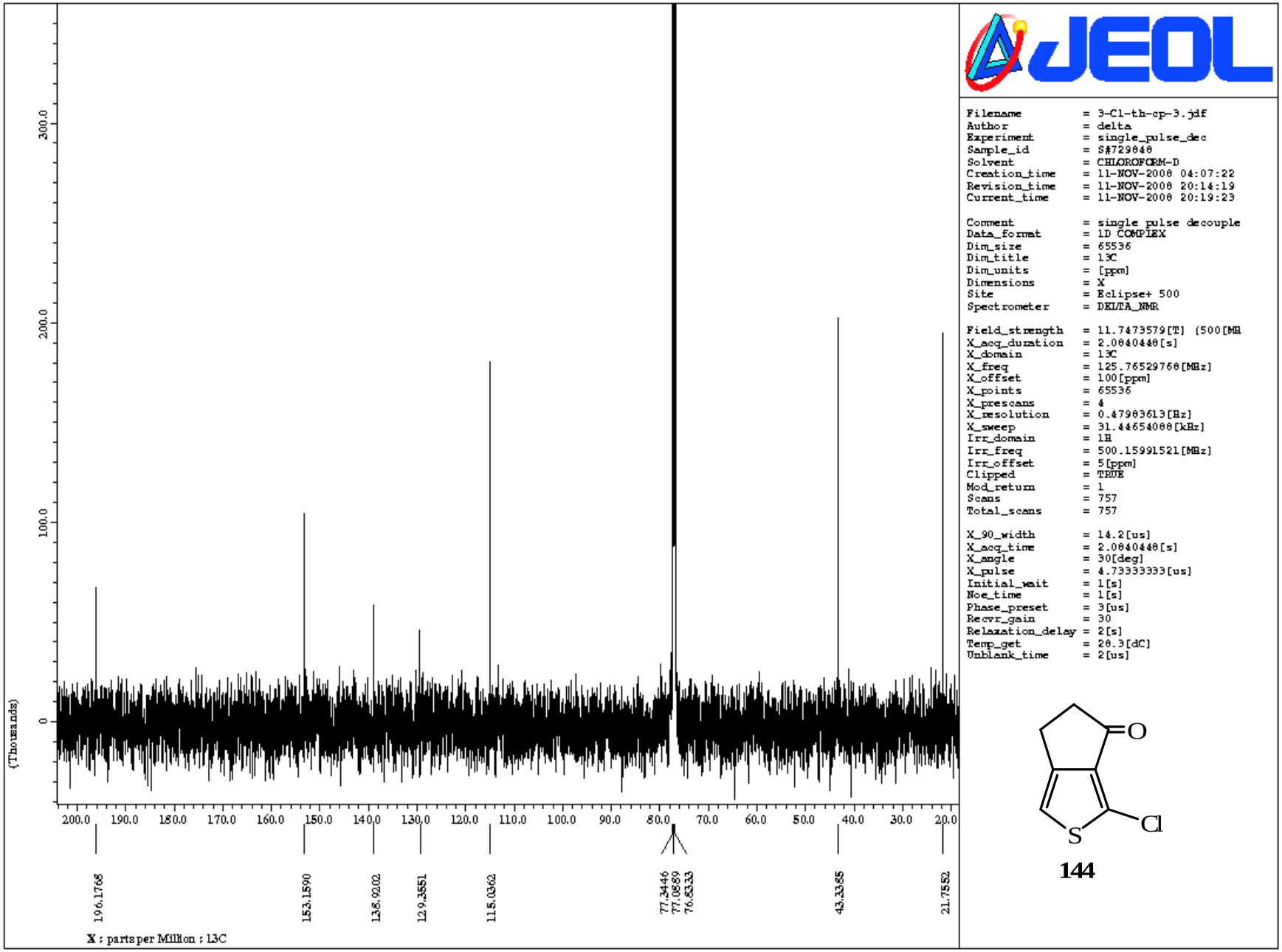
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 65536
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR

Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.0840448[s]
X_domain = 13C
X_freq = 125.76529768[MHz]
X_offset = 100[ppm]
X_points = 65536
X_prescans = 4
X_resolution = 0.47983613[Hz]
X_sweep = 31.44654088[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5[ppm]
Clipped = TRUE
Mod_return = 1
Scans = 757
Total_scans = 757

X_90_width = 14.2[us]
X_acq_time = 2.0840448[s]
X_angle = 30[deg]
X_pulse = 4.73333333[us]
Initial_wait = 1[s]
Noe_time = 1[s]
Phase_preset = 3[us]
Recvr_gain = 30
Relaxation_delay = 2[s]
Temp_get = 28.3[dC]
Unblank_time = 2[us]



144



JEOL

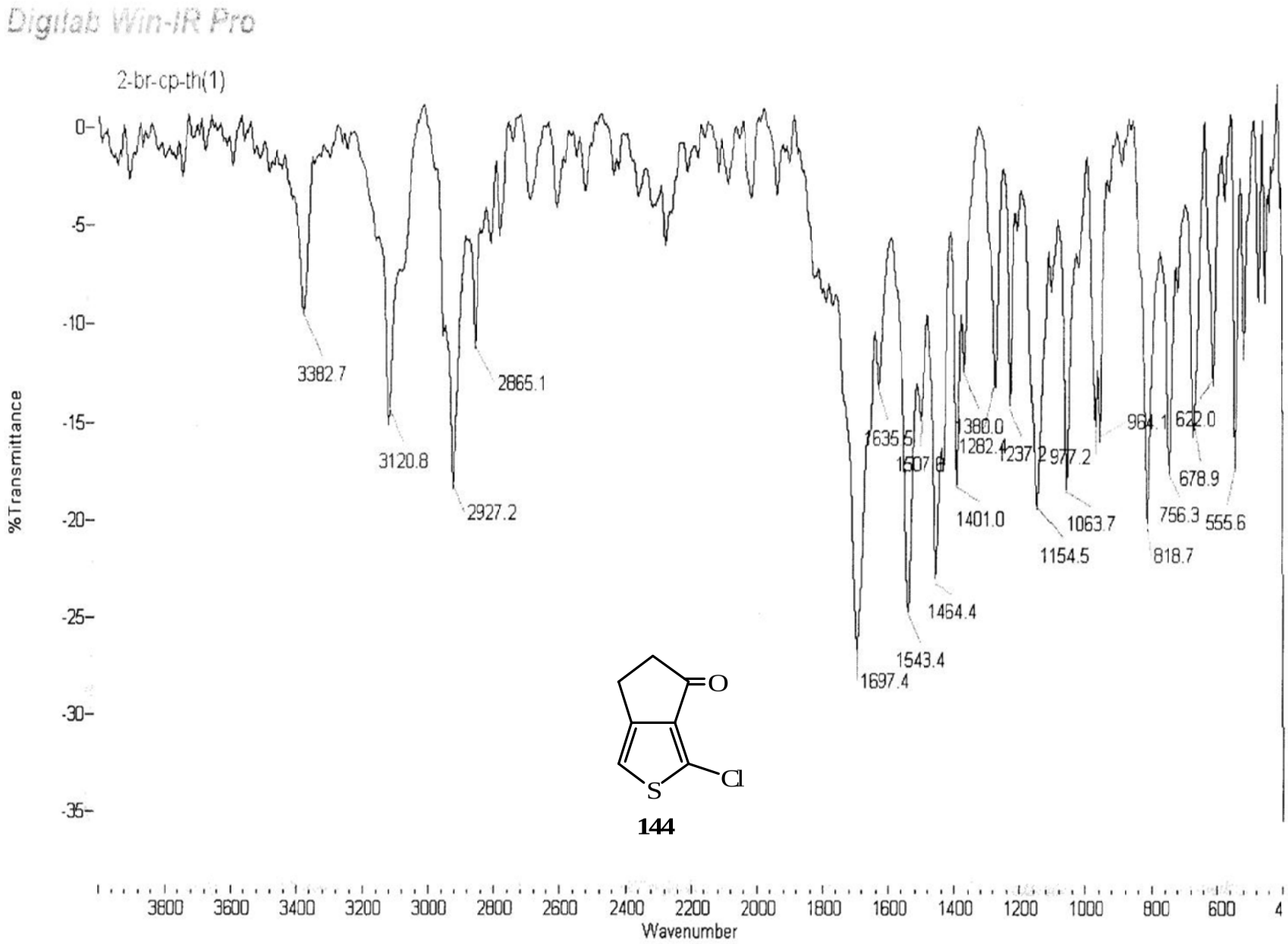
```
Filename          = 3-Cl-th-cp-3.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#729848
Solvent           = CHLOROFORM-D
Creation_time     = 11-NOV-2008 04:07:22
Revision_time     = 11-NOV-2008 20:14:19
Current_time      = 11-NOV-2008 20:19:23

Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 65536
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 2.0840448[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 65536
X_prescans        = 4
X_resolution      = 0.47983613[Hz]
X_sweep           = 31.44654088[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5[ppm]
Clipped           = TRUE
Mod_return        = 1
Scans             = 757
Total_scans       = 757

X_90_width        = 14.2[us]
X_acq_time        = 2.0840448[s]
X_angle           = 30[deg]
X_pulse           = 4.73333333[us]
Initial_wait      = 1[s]
Noe_time          = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 30
Relaxation_delay  = 2[s]
Temp_get          = 28.3[dC]
Unblank_time      = 2[us]
```

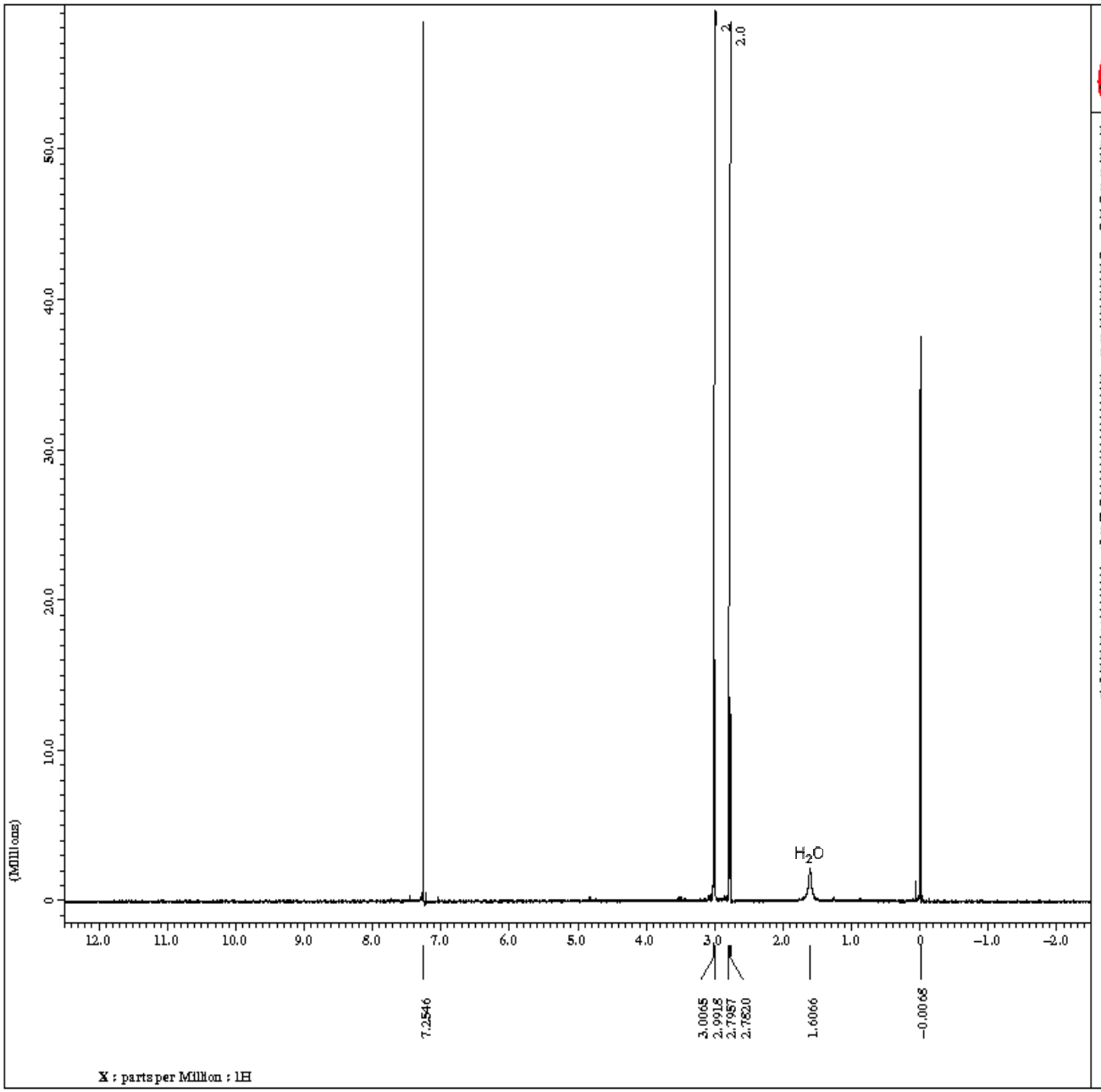

144


Digilab Win-IR Pro
2-br-cp-thi(1)
%Transmittance
0
-5
-10
-15
-20
-25
-30
-35
3382.7
3120.8
2927.2
2865.1
1697.4
1635.5
1607.8
1543.4
1464.4
1401.0
1380.0
1282.4
1237.2
1154.5
1063.7
977.2
964.1
818.7
756.3
678.9
622.0
555.6
O
Cl
S
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
4
Wavenumber

144

APPENDIX 23

^{1}H, ^{13}C NMR and IR spectra of 1-bromo-3-chloro-5,6-dihydrocyclopenta[*c*]thiophen-4-one (**147**)



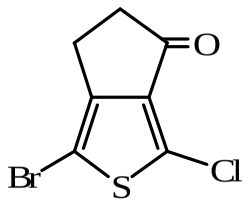
JEOL

```
Filename          = 1-br-3-cl-cp-thl-3.jd
Author            = delta
Experiment        = single_pulse.exp
Sample_id         = S#345574
Solvent           = CHLOROFORM-D
Creation_time     = 11-NOV-2008 16:23:31
Revision_time     = 11-NOV-2008 20:00:12
Current_time      = 11-NOV-2008 20:00:35

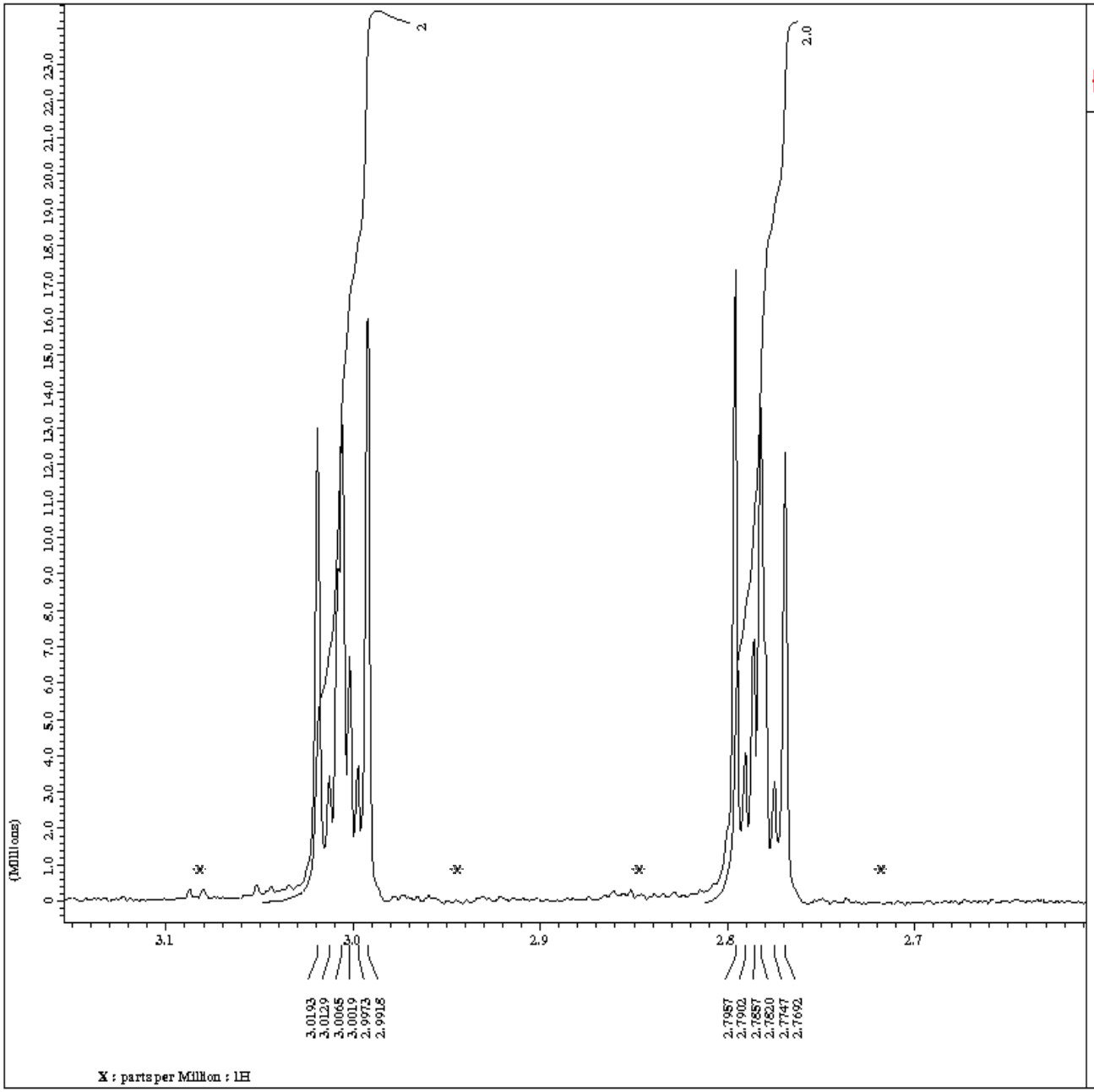
Comment           = Single Pulse Experime
Data_format       = 1D COMPLEX
Dim_size          = 16384
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

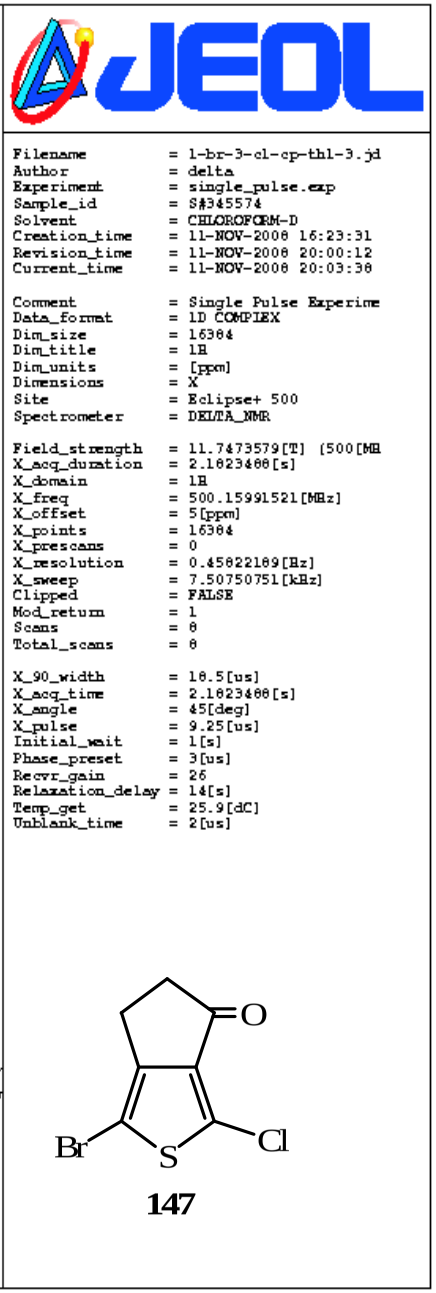
Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 2.1023488[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 5[ppm]
X_points          = 16384
X_prescans        = 0
X_resolution      = 0.45822189[Hz]
X_sweep           = 7.50750751[kHz]
Clipped           = FALSE
Mod_return        = 1
Scans             = 8
Total_scans       = 8

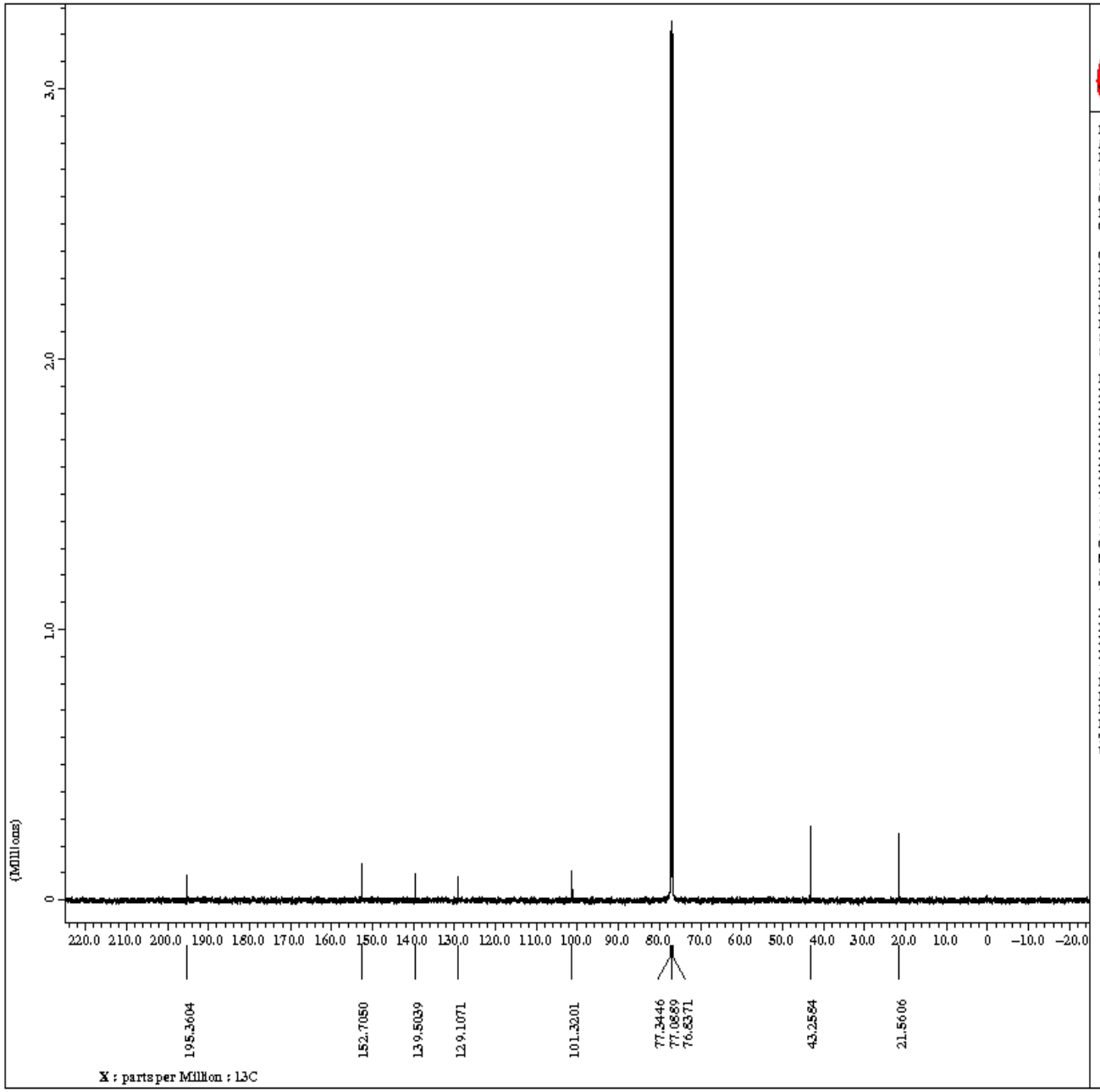
X_90_width        = 10.5[us]
X_acq_time        = 2.1023488[s]
X_angle           = 45[deg]
X_pulse           = 9.25[us]
Initial_wait      = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 26
Relaxation_delay  = 14[s]
Temp_get          = 25.9[dC]
Unblank_time      = 2[us]
```



147


(MMHoms)
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
15.0
16.0
17.0
18.0
19.0
20.0
21.0
22.0
23.0
3.1
3.0
2.9
2.8
2.7
3.0193
3.0129
3.0065
3.0019
2.9973
2.9918
2.7957
2.7902
2.7857
2.7820
2.7747
2.7692
X : parts per Million : 1H


JEOL
Filename = 1-br-3-cl-cp-thl-3.jd
Author = delta
Experiment = single_pulse.exp
Sample_id = S#345574
Solvent = CHLOROFORM-D
Creation_time = 11-NOV-2008 16:23:31
Revision_time = 11-NOV-2008 20:00:12
Current_time = 11-NOV-2008 20:03:30
Comment = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1023488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 10.5[us]
X_acq_time = 2.1023488[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 26
Relaxation_delay = 14[s]
Temp_get = 25.9[dC]
Unblank_time = 2[us]
O
Br
S
Cl
147

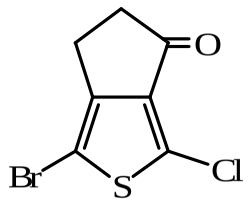


Filename = 1-Br-3-Cl-Th-Cp-2.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = S#853160
Solvent = CHLOROFORM-D
Creation_time = 19-OCT-2008 11:29:47
Revision_time = 19-OCT-2008 11:25:44
Current_time = 3-NOV-2008 10:15:32

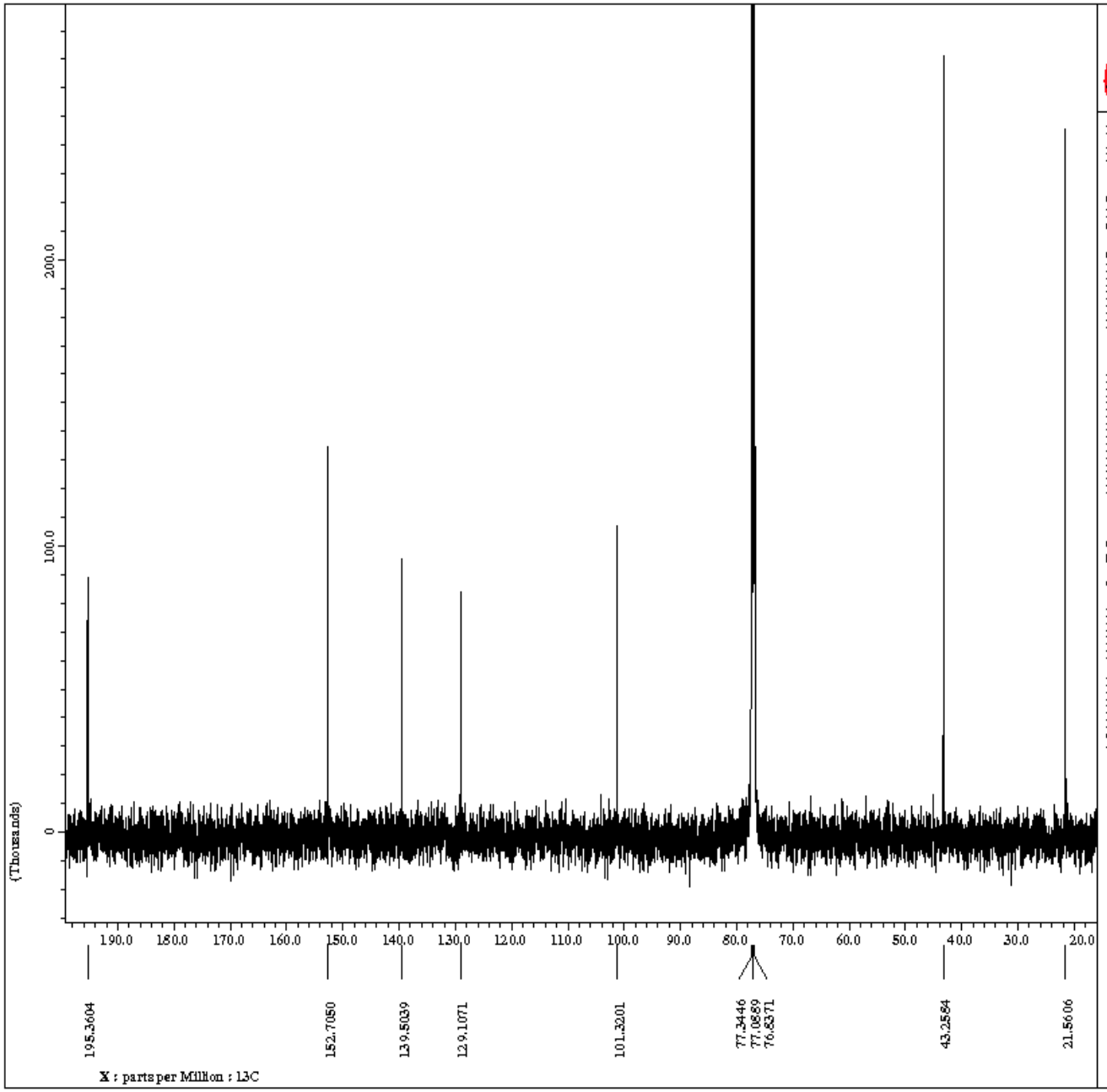
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 65536
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR

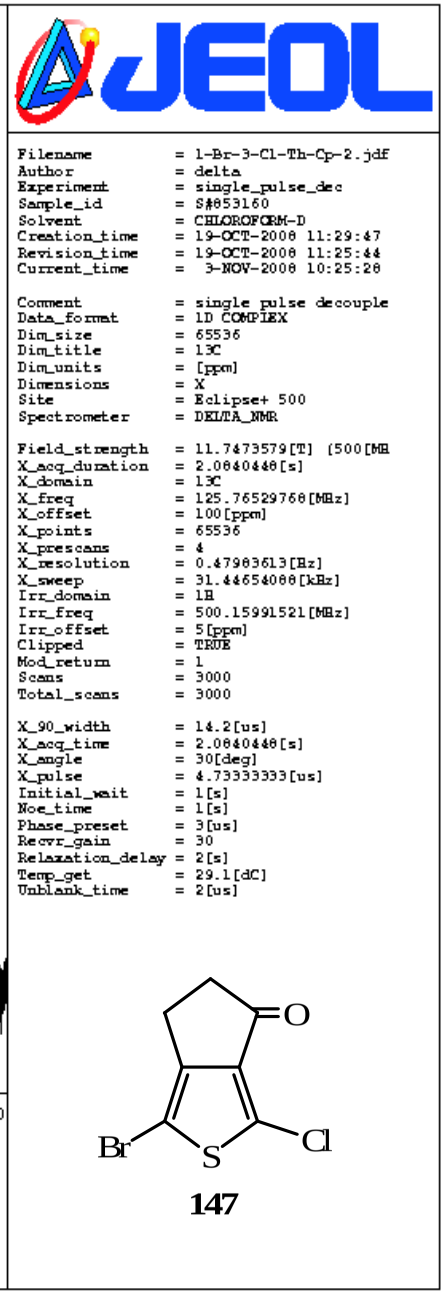
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.0840448[s]
X_domain = 13C
X_freq = 125.76529768[MHz]
X_offset = 100[ppm]
X_points = 65536
X_prescans = 4
X_resolution = 0.47983613[Hz]
X_sweep = 31.44654088[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5[ppm]
Clipped = TRUE
Mod_return = 1
Scans = 3000
Total_scans = 3000

X_90_width = 14.2[us]
X_acq_time = 2.0840448[s]
X_angle = 30[deg]
X_pulse = 4.73333333[us]
Initial_wait = 1[s]
Noe_time = 1[s]
Phase_preset = 3[us]
Recvr_gain = 30
Relaxation_delay = 2[s]
Temp_get = 29.1[dC]
Unblank_time = 2[us]



147





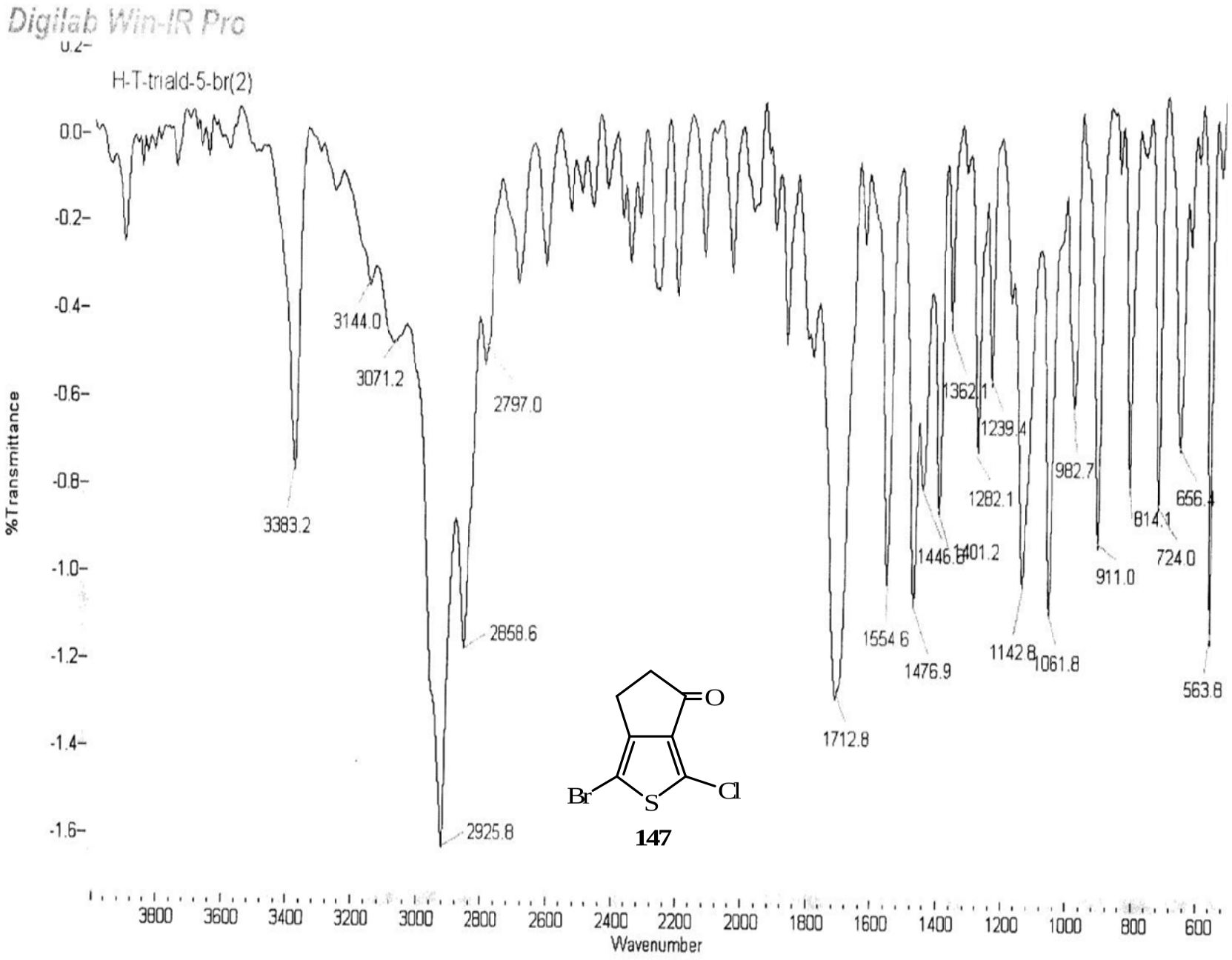
Filename = 1-Br-3-Cl-Th-Cp-2.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = S#853160
Solvent = CHLOROFORM-D
Creation_time = 19-OCT-2008 11:29:47
Revision_time = 19-OCT-2008 11:25:44
Current_time = 3-NOV-2008 10:25:20

Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 65536
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR

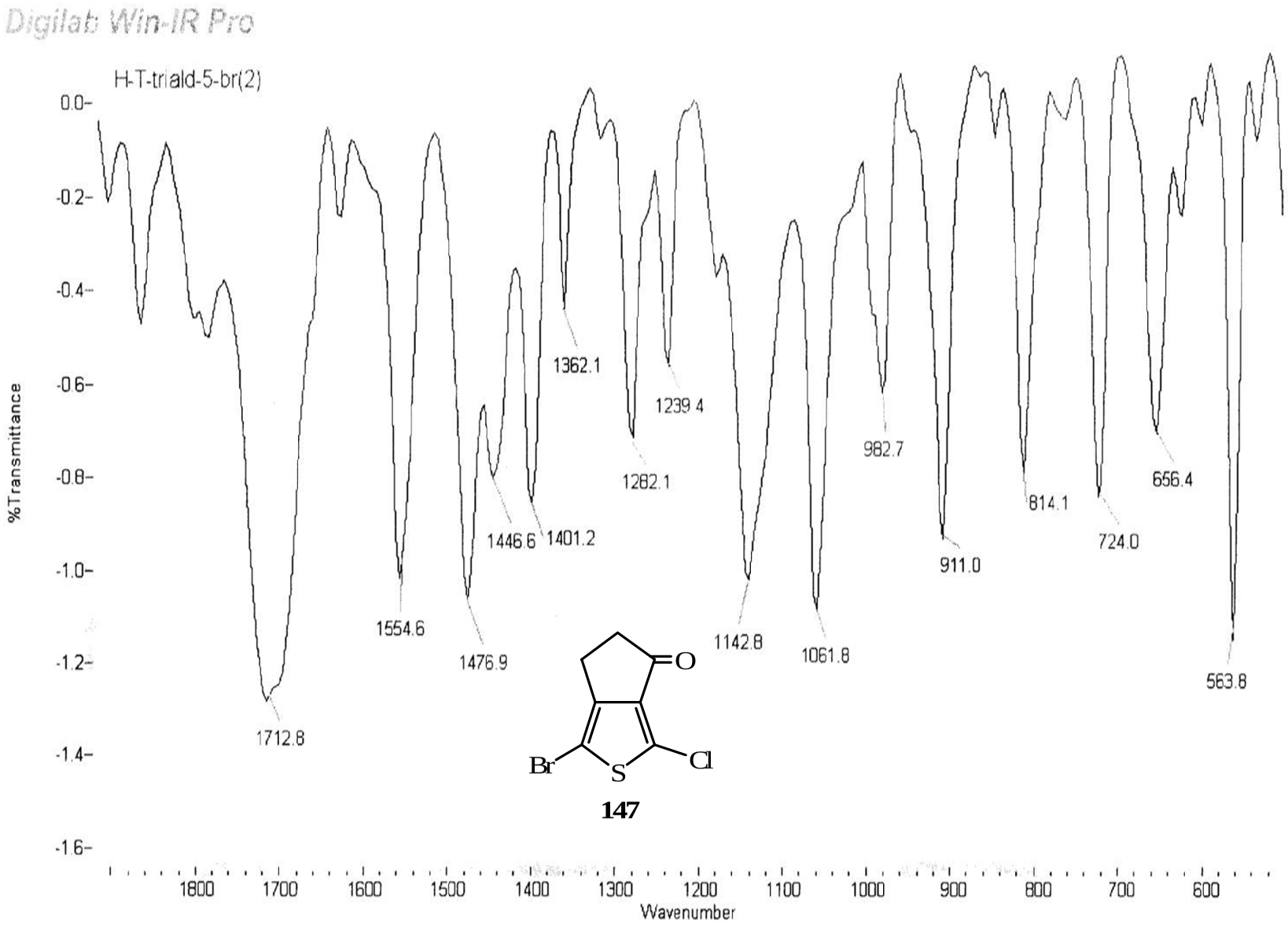
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.0840448[s]
X_domain = 13C
X_freq = 125.76529768[MHz]
X_offset = 100[ppm]
X_points = 65536
X_prescans = 4
X_resolution = 0.47903613[Hz]
X_sweep = 31.44654088[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5[ppm]
Clipped = TRUE
Mod_return = 1
Scans = 3000
Total_scans = 3000

X_90_width = 14.2[us]
X_acq_time = 2.0840448[s]
X_angle = 30[deg]
X_pulse = 4.73333333[us]
Initial_wait = 1[s]
Noe_time = 1[s]
Phase_preset = 3[us]
Recvr_gain = 30
Relaxation_delay = 2[s]
Temp_get = 29.1[dC]
Unblank_time = 2[us]

147


Digilab Win-IR Pro
H-T-triald-5-br(2)
%Transmittance
Wavenumber
3383.2
3144.0
3071.2
2925.8
2858.6
2797.0
1712.8
1554.6
1476.9
1446.8
1401.2
1362.1
1282.1
1239.4
1142.8
1061.8
982.7
911.0
814.1
724.0
656.4
563.8
O
Br
S
Cl

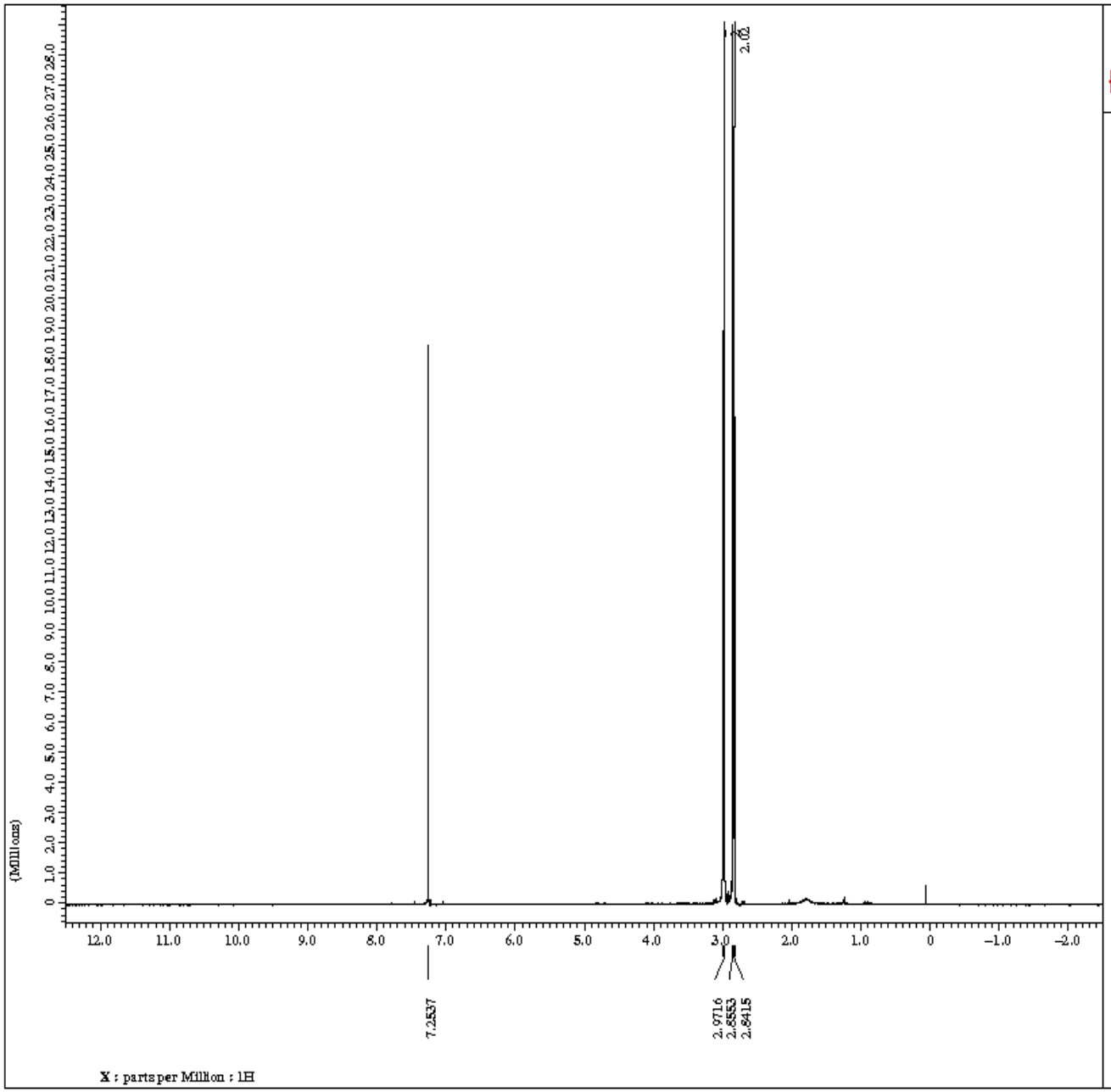
147


Digilab Win-IR Pro
H-T-triald-5-br(2)
%Transmittance
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
-1.4
-1.6
1712.8
1554.6
1476.9
1446.6
1401.2
1362.1
1282.1
1239.4
1142.8
1061.8
982.7
911.0
814.1
724.0
656.4
563.8
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
Wavenumber
O
Br
S
Cl

147

APPENDIX 24

^{1}H, ^{13}C NMR and IR spectra of 3-bromo-1-chloro-5,6-dihydrocyclopenta[*c*]thiophen-4-one (**148**)



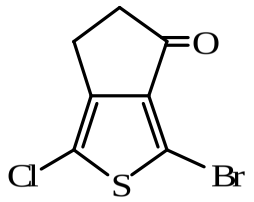
JEOL

```
Filename          = 3-Br-1-C-Th-cp-4.jdf
Author            = delta
Experiment        = single_pulse.exp
Sample_id         = S#479832
Solvent           = CHLOROFORM-D
Creation_time     = 17-OCT-2008 20:55:11
Revision_time     = 17-OCT-2008 13:27:45
Current_time      =  3-NOV-2008 11:12:36

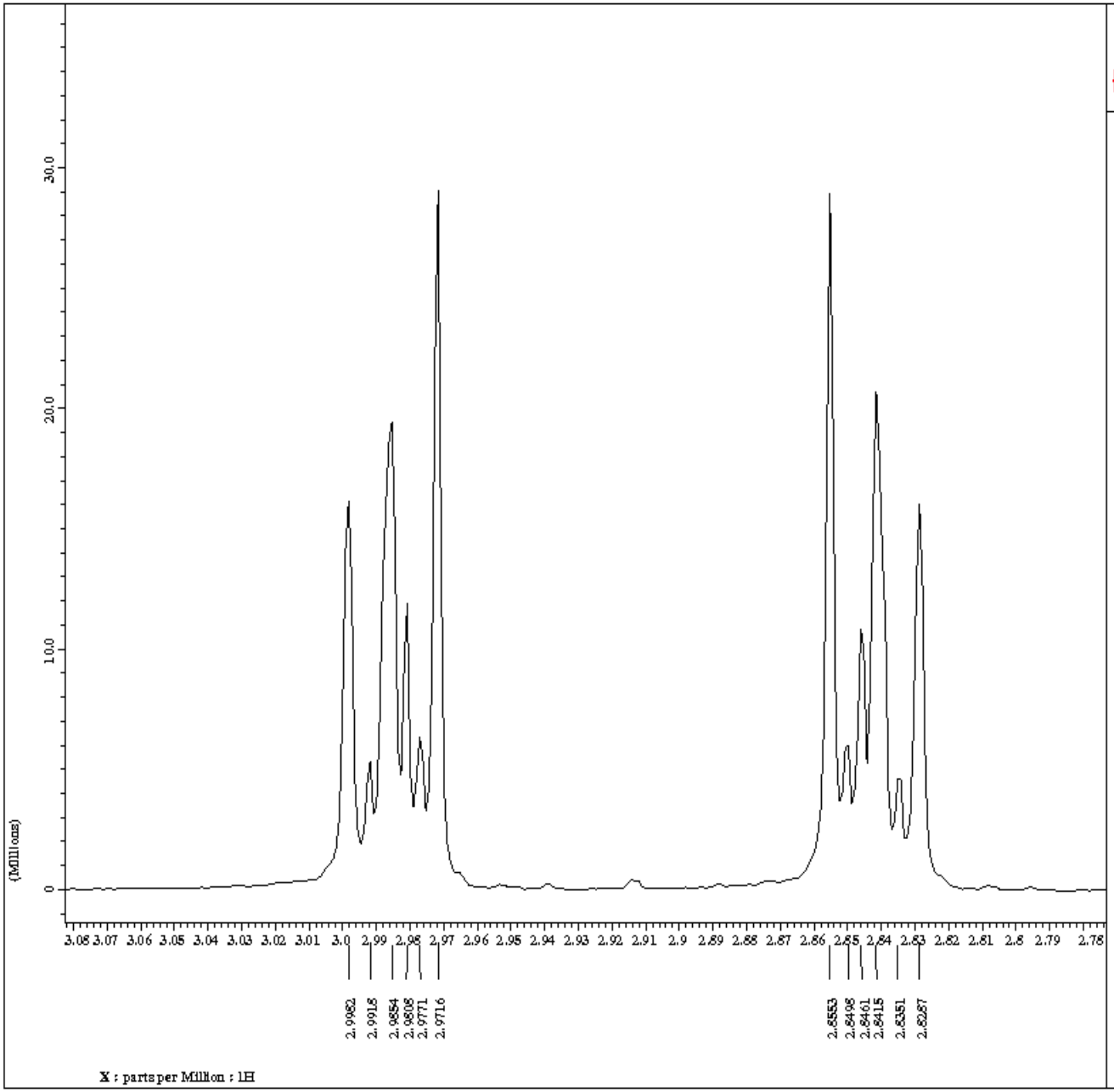
Comment           = Single Pulse Experime
Data_format       = 1D COMPLEX
Dim_size          = 16384
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 2.1823488[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 5[ppm]
X_points          = 16384
X_prescans        = 0
X_resolution      = 0.45822189[Hz]
X_sweep           = 7.50750751[kHz]
Clipped           = FALSE
Mod_return        = 1
Scans             = 8
Total_scans       = 8

X_90_width        = 10.5[us]
X_acq_time        = 2.1823488[s]
X_angle           = 45[deg]
X_pulse           = 9.25[us]
Initial_wait      = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 23
Relaxation_delay  = 14[s]
Temp_get          = 26[dC]
Unblank_time      = 2[us]
```



148

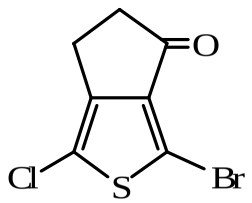


Filename = 3-Br-1-C-Th-cp-4.jdf
Author = delta
Experiment = single_pulse.exp
Sample_id = S#479032
Solvent = CHLOROFORM-D
Creation_time = 17-OCT-2008 20:55:11
Revision_time = 17-OCT-2008 13:27:45
Current_time = 3-NOV-2008 11:16:57

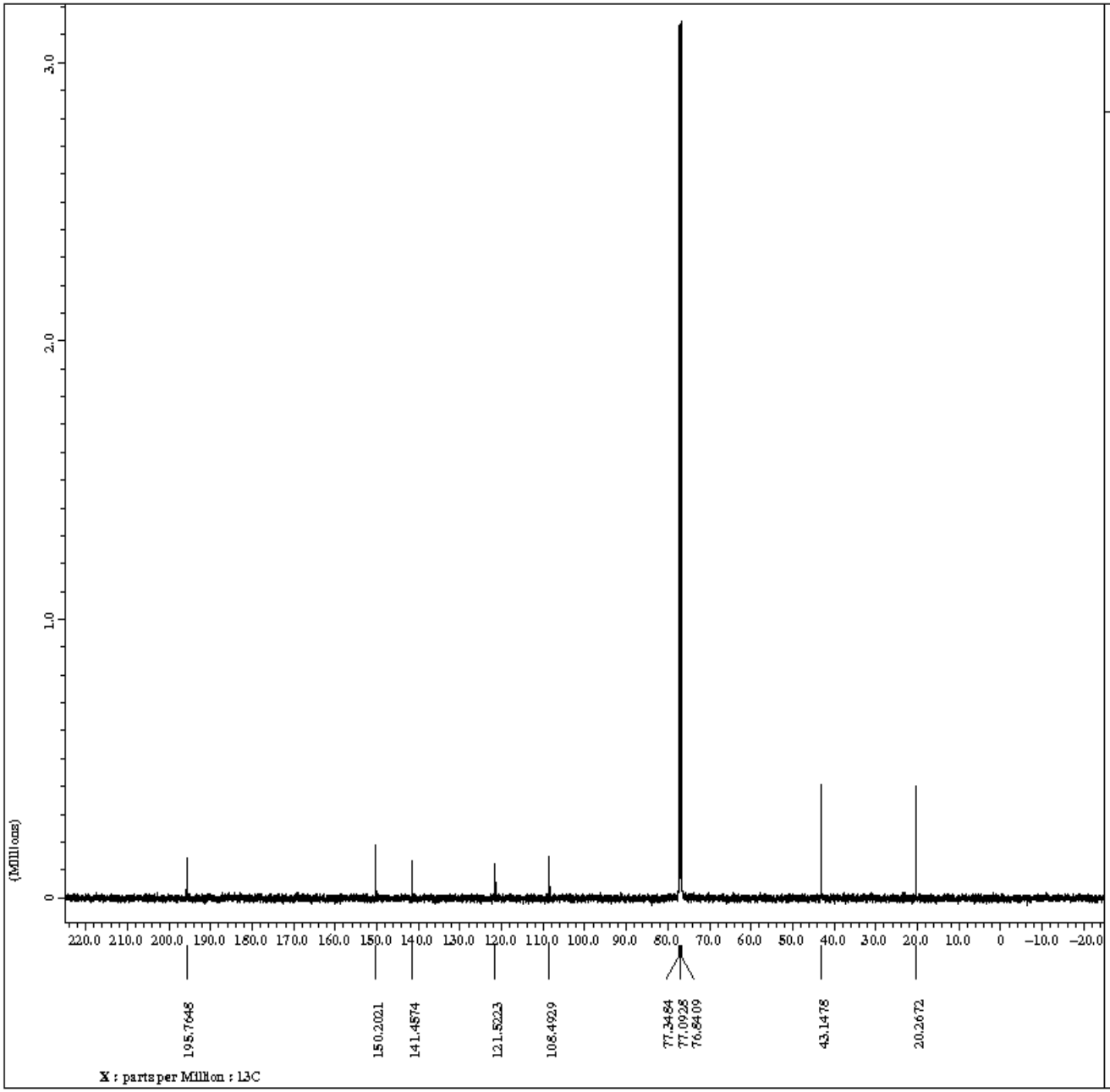
Comment = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR

Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1023488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8

X_90_width = 10.5[us]
X_acq_time = 2.1023488[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 23
Relaxation_delay = 14[s]
Temp_get = 26[dC]
Unblank_time = 2[us]



148



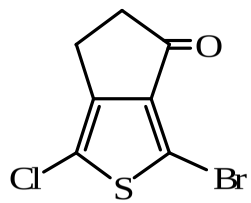
JEOL

```
Filename          = 3-Br-1-Cl-TH-Cp-3.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#402539
Solvent           = CHLOROFORM-D
Creation_time     = 17-OCT-2008 23:05:45
Revision_time     =  3-NOV-2008 10:06:58
Current_time      =  3-NOV-2008 10:09:15

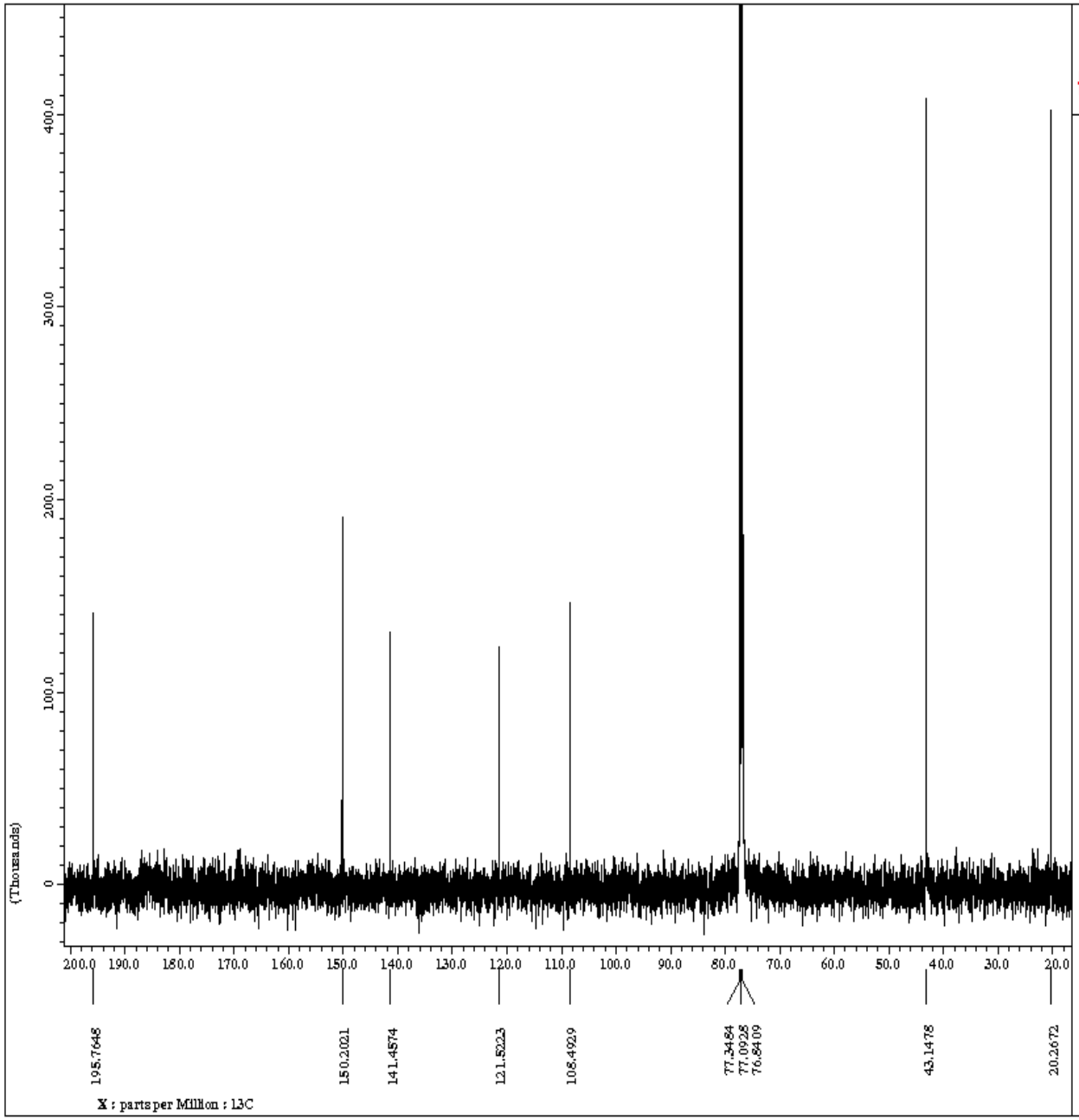
Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 65536
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

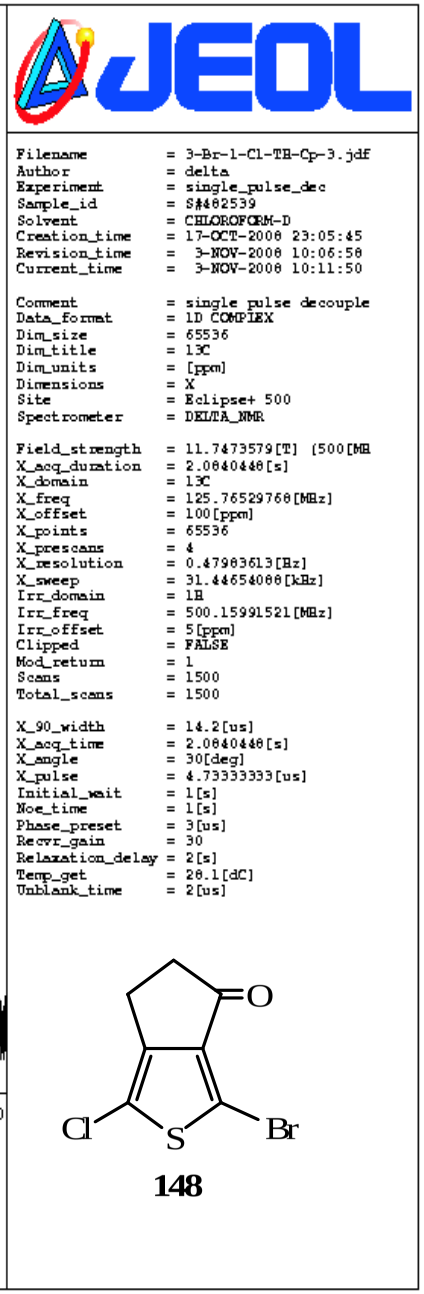
Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 2.0840448[s]
X_domain          = 13C
X_freq            = 125.76529760[MHz]
X_offset          = 100[ppm]
X_points          = 65536
X_prescans        = 4
X_resolution      = 0.47983613[Hz]
X_sweep           = 31.44654088[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 1500
Total_scans       = 1500

X_90_width        = 14.2[us]
X_acq_time        = 2.0840448[s]
X_angle           = 30[deg]
X_pulse           = 4.73333333[us]
Initial_wait      = 1[s]
Noe_time          = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 30
Relaxation_delay  = 2[s]
Temp_get          = 20.1[dC]
Unblank_time      = 2[us]
```

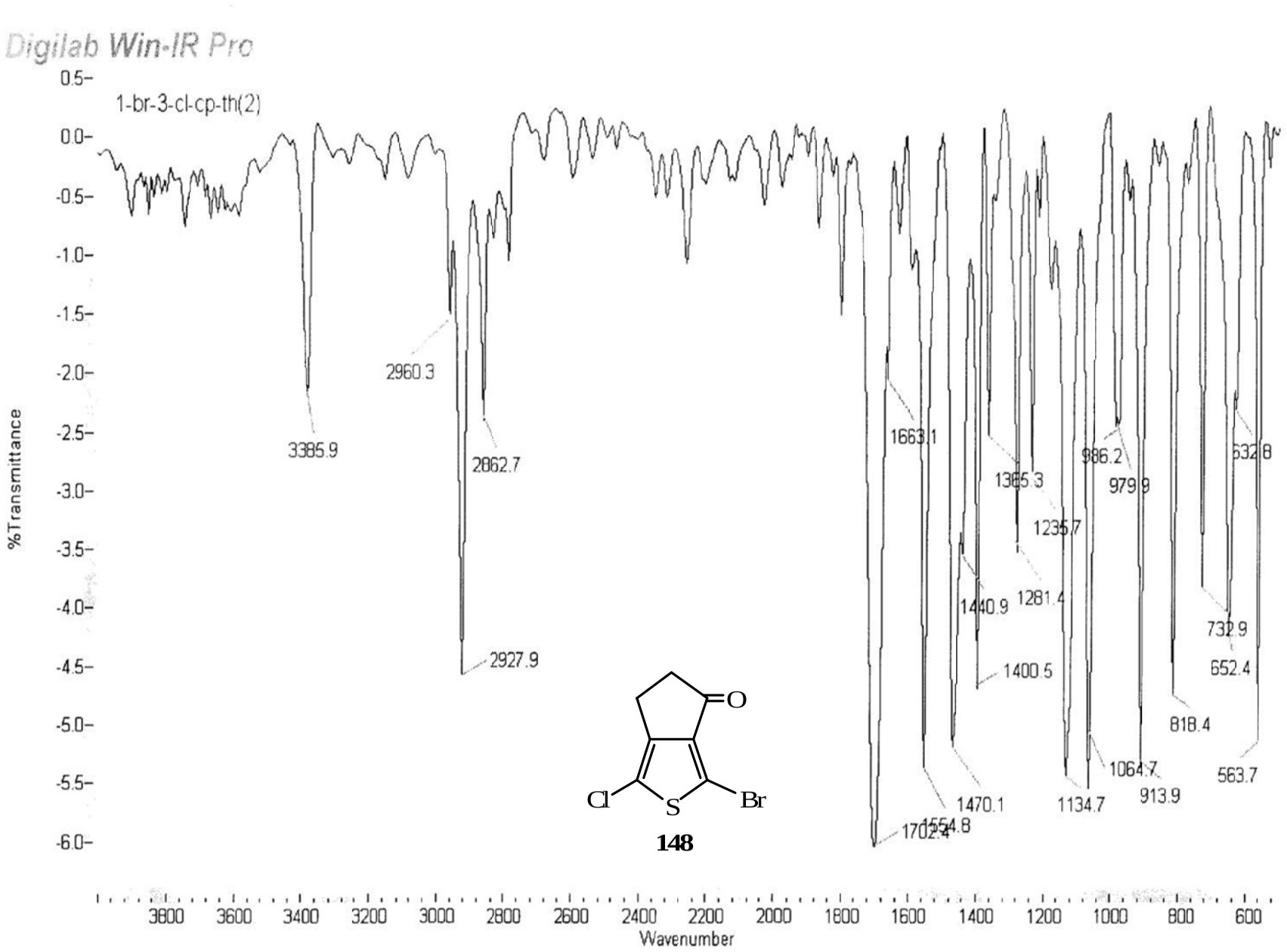


148

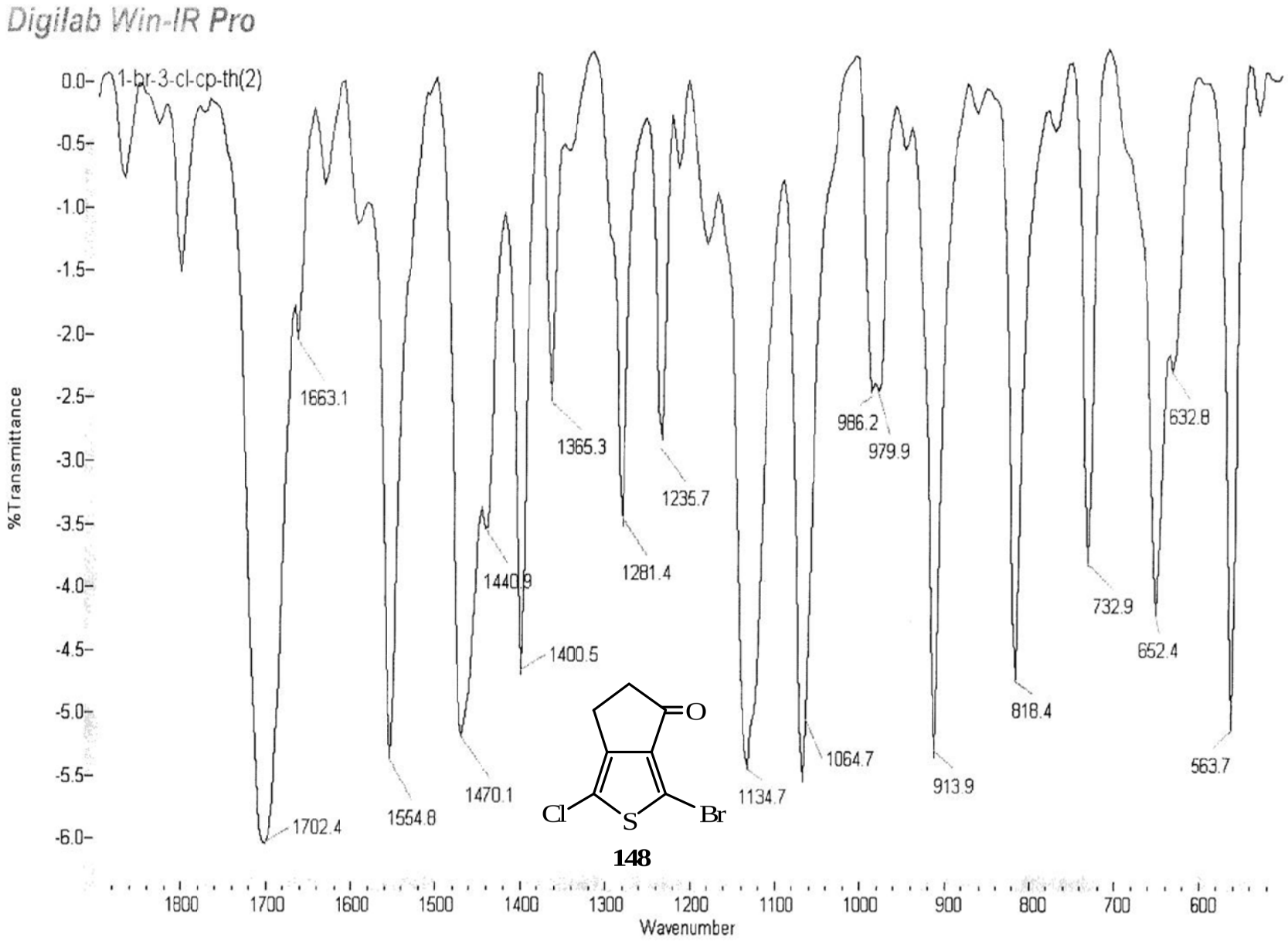

(Thousands)
400.0
300.0
200.0
100.0
0
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0
195.7648
150.2021
141.4574
121.5223
108.4929
77.3484
77.0928
76.8409
43.1478
20.2672
X : parts per Million : 13C


Filename = 3-Br-1-Cl-TH-Cp-3.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = S#402539
Solvent = CHLOROFORM-D
Creation_time = 17-OCT-2008 23:05:45
Revision_time = 3-NOV-2008 10:06:58
Current_time = 3-NOV-2008 10:11:50
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 65536
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.0840448[s]
X_domain = 13C
X_freq = 125.76529760[MHz]
X_offset = 100[ppm]
X_points = 65536
X_prescans = 4
X_resolution = 0.47983613[Hz]
X_sweep = 31.44654000[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 1500
Total_scans = 1500
X_90_width = 14.2[us]
X_acq_time = 2.0840448[s]
X_angle = 30[deg]
X_pulse = 4.73333333[us]
Initial_wait = 1[s]
Noe_time = 1[s]
Phase_preset = 3[us]
Recvr_gain = 30
Relaxation_delay = 2[s]
Temp_get = 28.1[dC]
Unblank_time = 2[us]
O
Cl
S
Br

148


Digilab Win-IR Pro
1-br-3-cl-cp-th(2)
%Transmittance
Wavenumber
3385.9
2960.3
2862.7
2927.9
1663.1
1554.8
1470.1
1440.9
1400.5
1385.3
1281.4
1235.7
1134.7
1064.7
986.2
979.9
913.9
818.4
732.9
652.4
632.8
563.7
O
Cl
S
Br

148

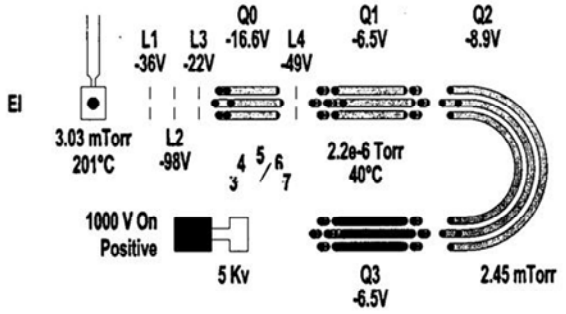

Digilab Win-IR Pro
1-br-3-cl-cp-th(2)
%Transmittance
Wavenumber
1663.1
1702.4
1554.8
1470.1
1440.9
1400.5
1365.3
1281.4
1235.7
1134.7
1064.7
986.2
979.9
913.9
818.4
732.9
652.4
632.8
563.7
O
Cl
S
Br

148

APPENDIX 25

MS spectra of 3,3'-dichloro-4,4',5,5'-tetrahydro-1,1'-bi(cyclopenta[*c*]thiophene)-4,6'-dione (**151**)

Tune: FC-43 EI (9 Aug 2007) Scan: Current Scan



1200:Acquiring 3.1 Min

Readbacks

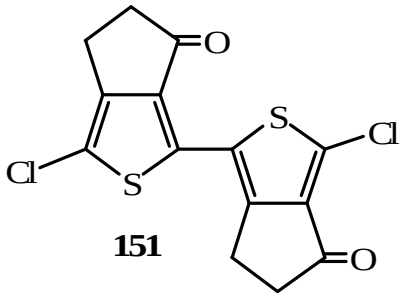
51:	-8.00	V	Q1 Ion Guide
52:	-0.21	V	Lens Spare A
53:	-5.54	V	Q3 Ion Guide
54:	0.62	V	Lens Spare B
55:	3.01	mtorr	EI/CI Source Pressure
56:	2.45	mtorr	Collision Pressure
57:	760.00	Torr	Forepump Pressure
58:	36.18	mtorr	Auxiliary Pressure
59:	-0.39	ma	Total Valve Current
60:	10.90	V	Vent Valve Lower Drive
61:	193.36	ua	Filament Emission Current
62:	3.88	V	Filament Emission Current Set Point
63:	1.44	V	Detector Set Point
64:	99.02	%	Full Turbo Speed
65:	0.01	V	User Out 1
66:	0.01	V	User Out 2
67:	0.01	V	User In 1
68:	0.01	V	User In 2
69:	0.01	V	User In 3
70:	0.01	V	DI Voltage Set Point
71:	-5.00		Unused ESI Serial Dac
72:	23.59	V	DI Voltage
73:	2.32	uA	DI Current
74:	-1.89	V	Control of +162V P.S.
75:	-1.65	V	Control of -162V P.S.
76:	0.04	V	EI/CI Source Heater Voltage
77:	0.00	mA	EI/CI Source Heater Current
78:	0.07	V	Auxiliary Heater Voltage
79:	1.95	mA	Auxiliary Heater Current
80:	200.00	deg C	Auxiliary Heater Temperature

acquiring Profile to C:\VarianWS\data\my files\AUG 9 2007 16-09

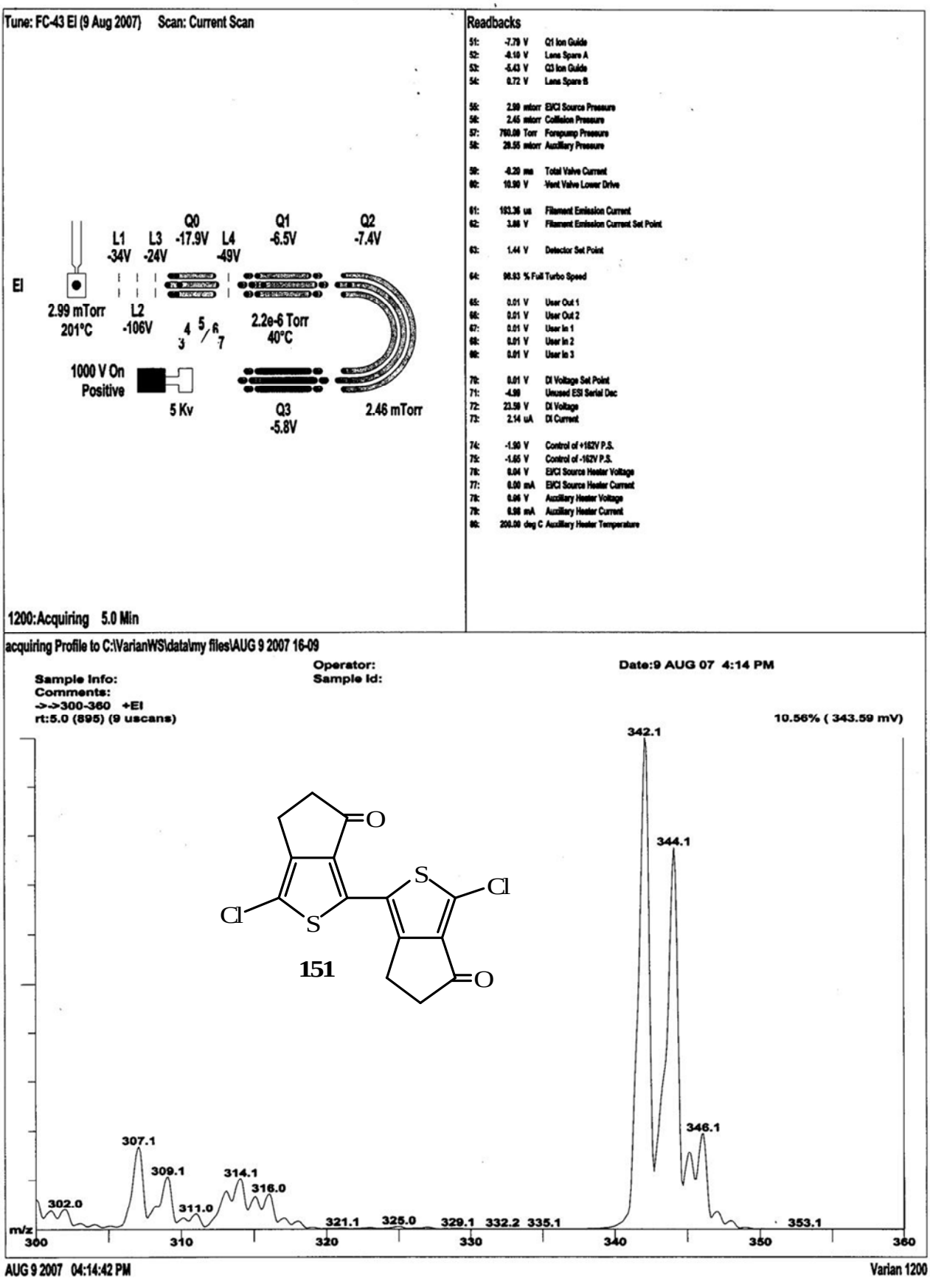
Operator:
Sample Id:

Date:9 AUG 07 4:12 PM

Sample Info:
Comments:
->->50-400 +EI
rt:3.1 (543)

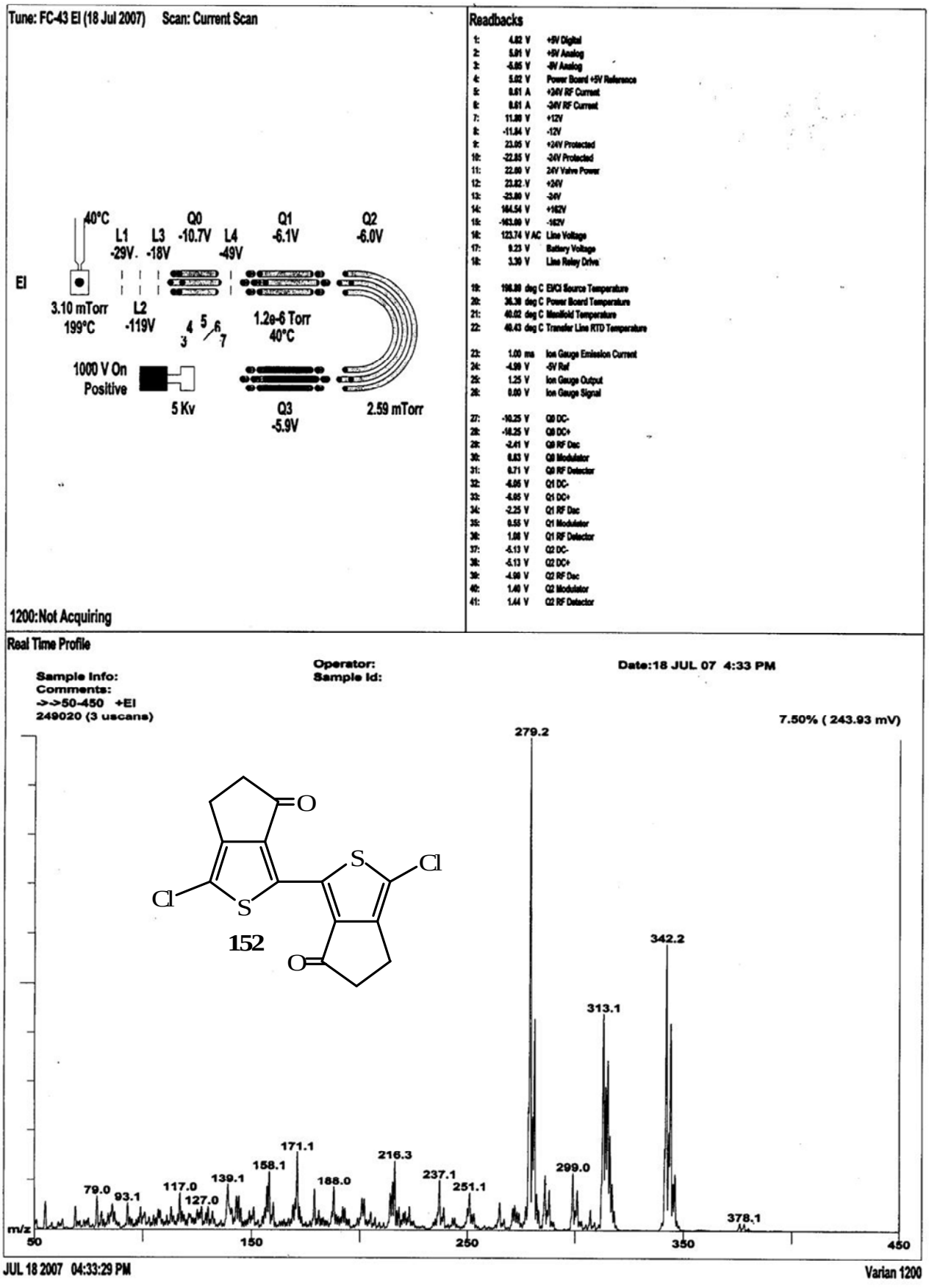


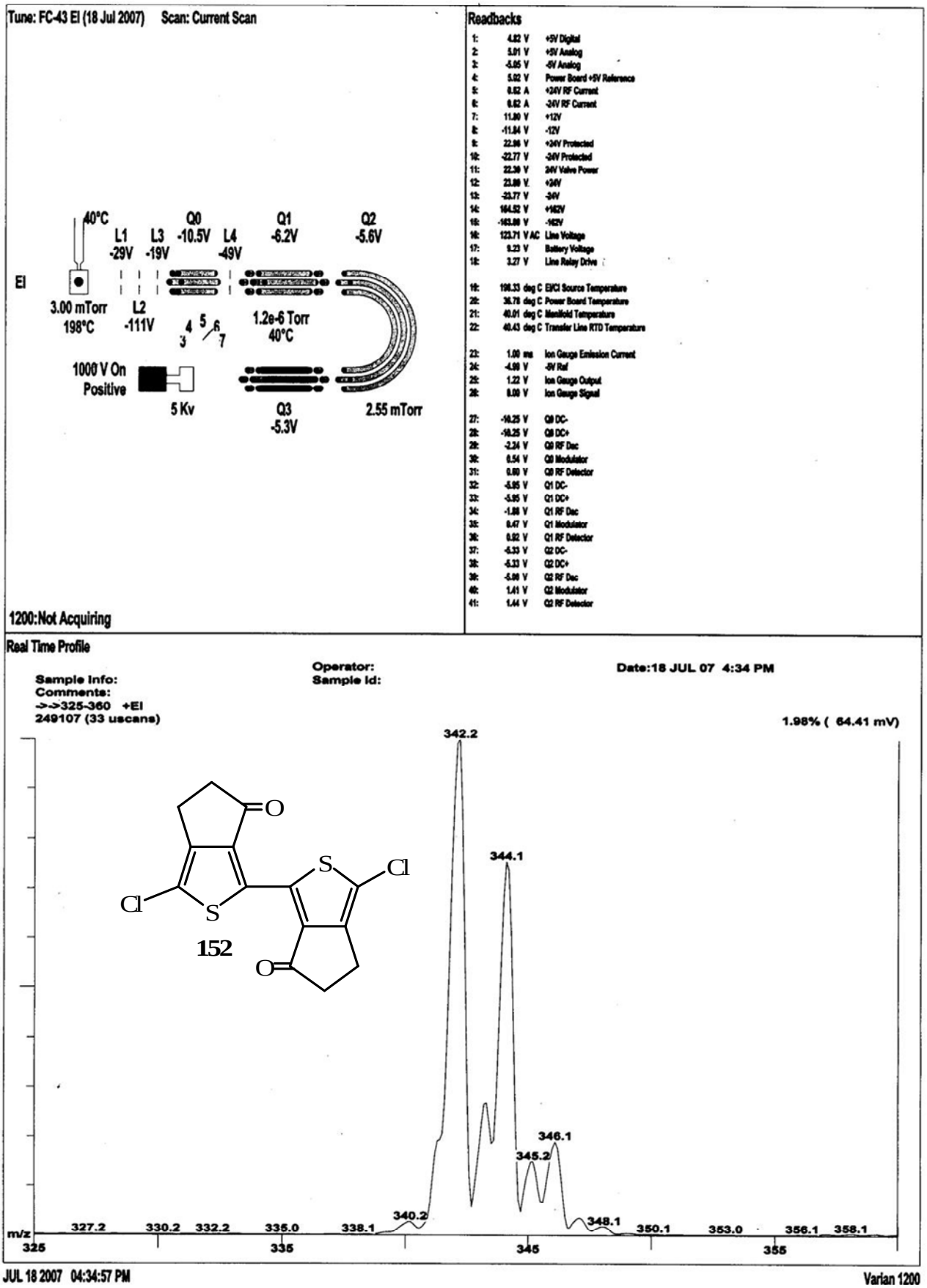
151


Tune: FC-43 EI (9 Aug 2007) Scan: Current Scan
Readbacks
51: -7.79 V Q1 Ion Guide
52: -8.19 V Lens Spare A
53: -5.43 V Q3 Ion Guide
54: 0.72 V Lens Spare B
56: 2.99 mtorr EI/CI Source Pressure
56: 2.45 mtorr Collision Pressure
57: 760.00 Torr Forepump Pressure
58: 29.55 mtorr Auxiliary Pressure
59: -0.20 ma Total Valve Current
60: 10.90 V Vent Valve Lower Drive
61: 183.36 ua Filament Emission Current
62: 3.88 V Filament Emission Current Set Point
63: 1.44 V Detector Set Point
64: 98.93 % Full Turbo Speed
65: 0.01 V User Out 1
66: 0.01 V User Out 2
67: 0.01 V User In 1
68: 0.01 V User In 2
69: 0.01 V User In 3
70: 0.01 V DI Voltage Set Point
71: -4.90 Unused ESI Serial Dac
72: 23.59 V DI Voltage
73: 2.14 uA DI Current
74: -1.90 V Control of +162V P.S.
75: -1.65 V Control of -162V P.S.
76: 0.04 V EI/CI Source Heater Voltage
77: 0.00 mA EI/CI Source Heater Current
78: 0.06 V Auxiliary Heater Voltage
79: 0.98 mA Auxiliary Heater Current
80: 200.00 deg C Auxiliary Heater Temperature
Q0 -17.9V
Q1 -6.5V
Q2 -7.4V
L1 -34V
L3 -24V
L4 -49V
EI
2.99 mTorr 201°C
L2 -106V
2.2e-6 Torr 40°C
1000 V On Positive
5 Kv
Q3 -5.8V
2.46 mTorr
1200:Acquiring 5.0 Min
acquiring Profile to C:\VarianWS\data\my files\AUG 9 2007 16-09
Operator:
Sample Id:
Date:9 AUG 07 4:14 PM
Sample Info:
Comments:
->->300-360 +EI
rt:5.0 (895) (9 uscans)
10.56% (343.59 mV)
O
S
Cl
Cl
S
O
151
342.1
344.1
346.1
307.1
309.1
314.1
316.0
311.0
302.0
321.1
325.0
329.1
332.2
335.1
353.1
m/z
300
310
320
330
340
350
360
AUG 9 2007 04:14:42 PM
Varian 1200

APPENDIX 26

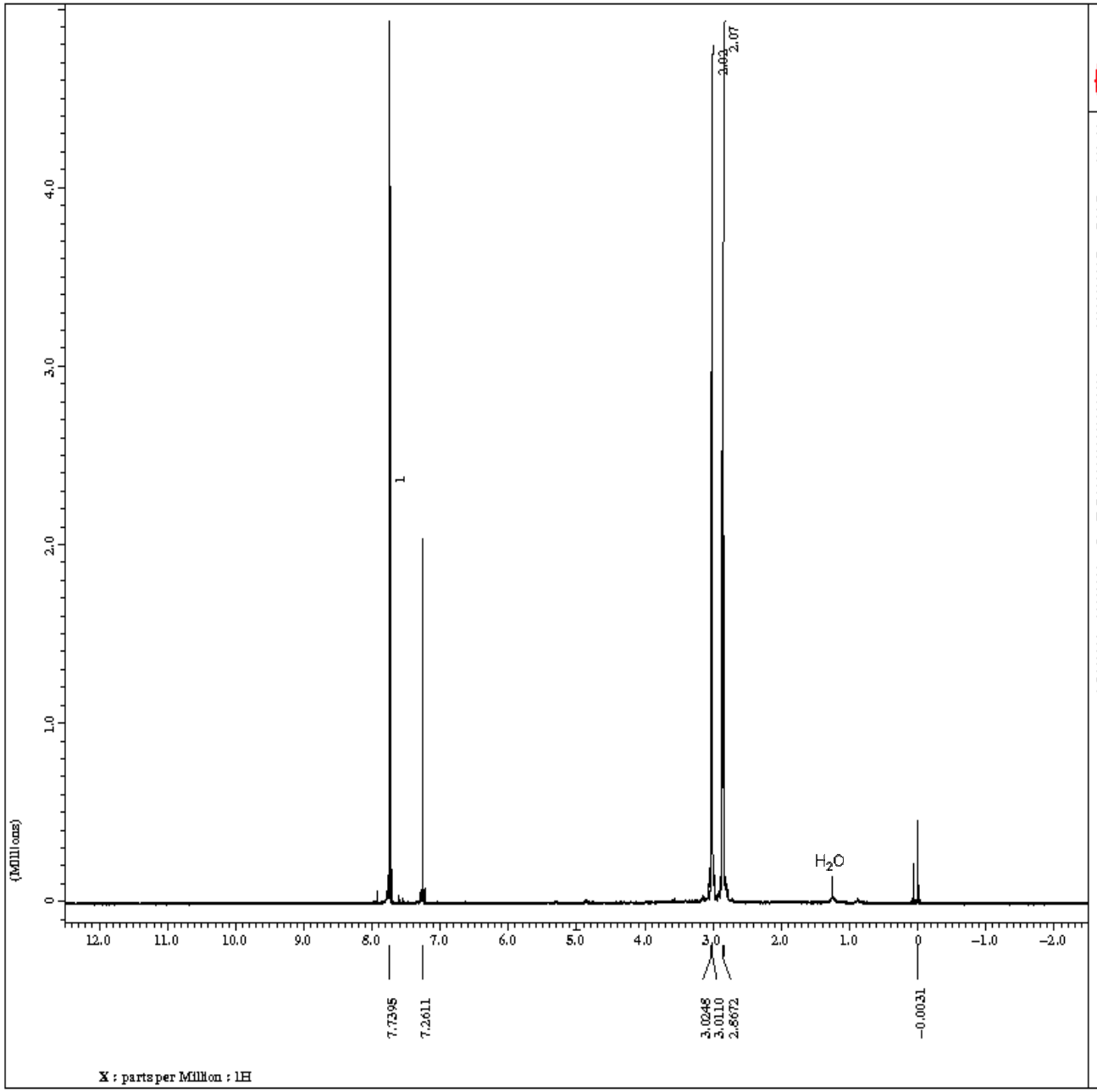
MS spectra of 3,3'-dichloro-4,4',5,5'-tetrahydro-1,1'-bi(cyclopenta[*c*]thiophene)-6,6'-dione (**152**)


Tune: FC-43 EI (18 Jul 2007) Scan: Current Scan
40°C
L1 -29V
L3 -18V
Q0 -10.7V
L4 -49V
Q1 -6.1V
Q2 -6.0V
EI
3.10 mTorr
199°C
L2 -119V
1.2e-6 Torr
40°C
1000 V On
Positive
5 Kv
Q3 -5.9V
2.59 mTorr
1200:Not Acquiring
Readbacks
1: 4.82 V +5V Digital
2: 5.01 V +5V Analog
3: -5.05 V -5V Analog
4: 5.02 V Power Board +5V Reference
5: 8.61 A +24V RF Current
6: 8.61 A -24V RF Current
7: 11.88 V +12V
8: -11.84 V -12V
9: 23.05 V +24V Protected
10: -22.85 V -24V Protected
11: 22.80 V 24V Valve Power
12: 23.82 V +24V
13: -23.80 V -24V
14: 164.54 V +162V
15: -163.00 V -162V
16: 123.74 V AC Line Voltage
17: 9.23 V Battery Voltage
18: 3.30 V Line Relay Drive
19: 196.88 deg C EICI Source Temperature
20: 36.38 deg C Power Board Temperature
21: 40.02 deg C Manifold Temperature
22: 40.43 deg C Transfer Line RTD Temperature
23: 1.00 ma Ion Gauge Emission Current
24: -4.99 V -5V Ref
25: 1.25 V Ion Gauge Output
26: 0.00 V Ion Gauge Signal
27: -10.25 V Q0 DC-
28: -10.25 V Q0 DC+
29: -2.41 V Q0 RF Dac
30: 8.83 V Q0 Modulator
31: 0.71 V Q0 RF Detector
32: -6.05 V Q1 DC-
33: -6.05 V Q1 DC+
34: -2.25 V Q1 RF Dac
35: 0.55 V Q1 Modulator
36: 1.08 V Q1 RF Detector
37: -5.13 V Q2 DC-
38: -5.13 V Q2 DC+
39: -4.99 V Q2 RF Dac
40: 1.40 V Q2 Modulator
41: 1.44 V Q2 RF Detector
Real Time Profile
Sample Info:
Comments:
->->50-450 +EI
249020 (3 uscans)
Operator:
Sample Id:
Date:18 JUL 07 4:33 PM
7.50% (243.93 mV)
O
S
Cl
Cl
S
O
152
279.2
342.2
313.1
171.1
158.1
216.3
237.1
299.0
139.1
188.0
251.1
117.0
127.0
79.0
93.1
378.1
m/z
50
150
250
350
450
JUL 18 2007 04:33:29 PM
Varian 1200


Tune: FC-43 EI (18 Jul 2007) Scan: Current Scan
40°C
L1 -29V
L3 -19V
Q0 -10.5V
L4 -49V
Q1 -6.2V
Q2 -5.6V
EI
3.00 mTorr
198°C
L2 -111V
1.2e-6 Torr
40°C
1000 V On
Positive
5 Kv
Q3 -5.3V
2.55 mTorr
1200:Not Acquiring
Readbacks
1: 4.82 V +5V Digital
2: 5.01 V +5V Analog
3: -5.05 V -5V Analog
4: 5.02 V Power Board +5V Reference
5: 0.62 A +24V RF Current
6: 0.62 A -24V RF Current
7: 11.90 V +12V
8: -11.84 V -12V
9: 22.96 V +24V Protected
10: -22.77 V -24V Protected
11: 22.39 V 24V Valve Power
12: 23.89 V +24V
13: -23.77 V -24V
14: 164.52 V +162V
15: -163.88 V -162V
16: 123.71 V AC Line Voltage
17: 9.23 V Battery Voltage
18: 3.27 V Line Relay Drive
19: 198.33 deg C EI/CI Source Temperature
20: 36.78 deg C Power Board Temperature
21: 40.01 deg C Manifold Temperature
22: 40.43 deg C Transfer Line RTD Temperature
23: 1.00 ma Ion Gauge Emission Current
24: -4.99 V -5V Ref
25: 1.22 V Ion Gauge Output
26: 0.00 V Ion Gauge Signal
27: -10.25 V Q0 DC-
28: -10.25 V Q0 DC+
29: -2.24 V Q0 RF Dac
30: 0.54 V Q0 Modulator
31: 0.00 V Q0 RF Detector
32: -5.95 V Q1 DC-
33: -5.95 V Q1 DC+
34: -1.88 V Q1 RF Dac
35: 0.47 V Q1 Modulator
36: 0.02 V Q1 RF Detector
37: -5.33 V Q2 DC-
38: -5.33 V Q2 DC+
39: -5.00 V Q2 RF Dac
40: 1.41 V Q2 Modulator
41: 1.44 V Q2 RF Detector
Real Time Profile
Operator:
Sample Id:
Date:18 JUL 07 4:34 PM
Sample Info:
Comments:
->->325-360 +EI
249107 (33 uscans)
1.98% (64.41 mV)
342.2
344.1
346.1
345.2
340.2
348.1
O
S
Cl
Cl
S
O
152
m/z
325
327.2
330.2
332.2
335.0
338.1
335
345
350.1
353.0
355
356.1
358.1
JUL 18 2007 04:34:57 PM
Varian 1200

APPENDIX 27

^{1}H, ^{13}C NMR and IR spectra of 1-bromo-5,6-dihydrocyclopenta[*c*]thiophen-4-one (**153**)



JEOL

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Author	= delta
Experiment	= single_pulse.exp
Sample_id	= S#461760
Solvent	= CHLOROFORM-D
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Revision_time	= 9-NOV-2008 19:35:53
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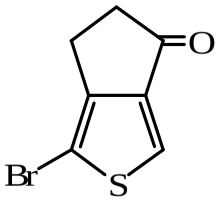
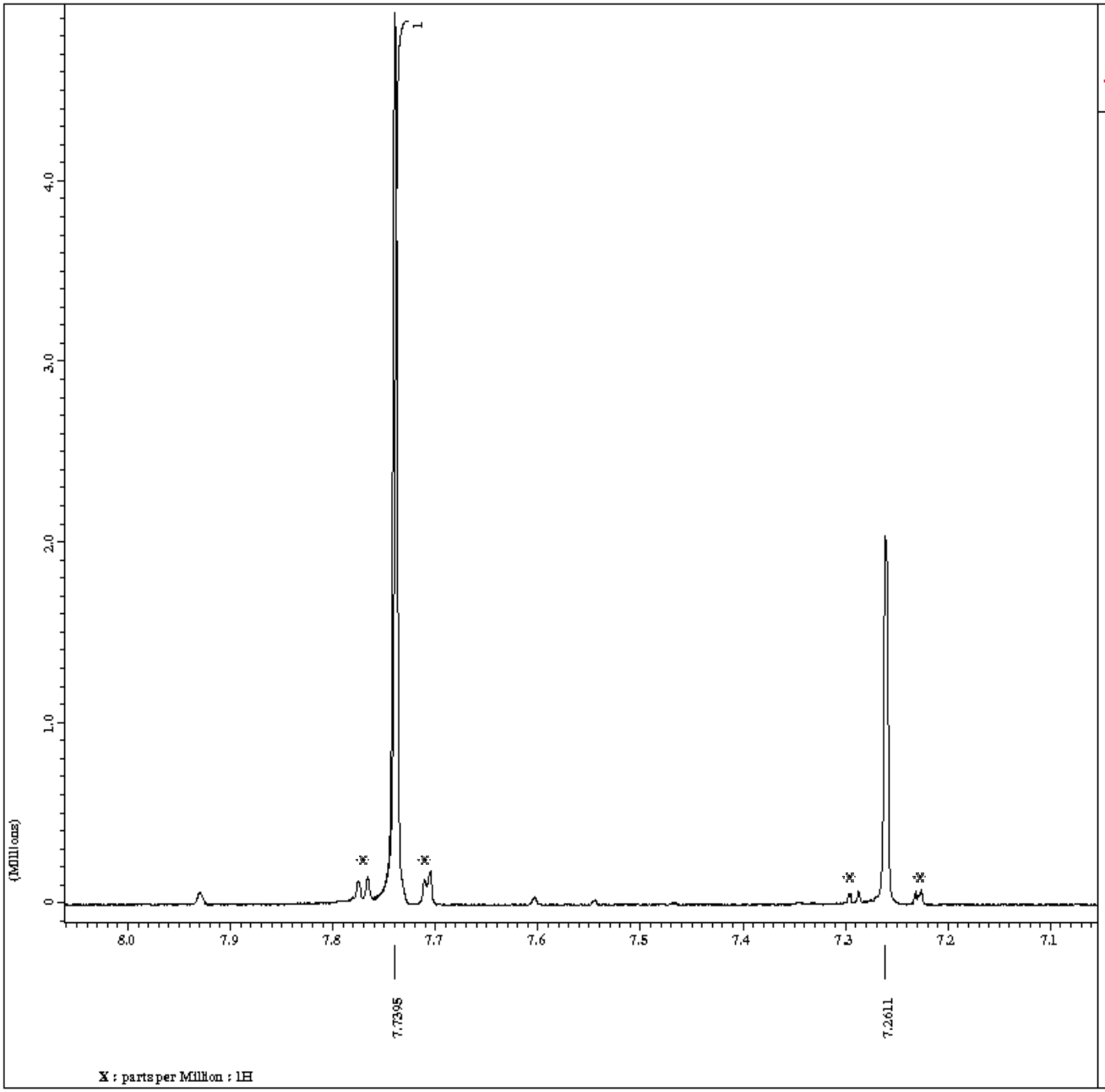
Data_format	= 1D COMPLEX
Dim_size	= 65536
Dim_title	= 1H
Dim_units	= [ppm]
Dimensions	= X
Site	= Eclipse+ 500
Spectrometer	= DELTA_NMR
Field_strength	= 11.7473579[T] (500[MH
X_acq_duration	= 0.7293952[s]
X_domain	= 1H
X_freq	= 500.15991521[MHz]
X_offset	= 5[ppm]
X_points	= 65536
X_prescans	= 0
X_resolution	= 0.11455547[Hz]
X_sweep	= 7.50750751[kHz]
Clipped	= FALSE
Mod_return	= 1
Scans	= 8
Total_scans	= 8
X_90_width	= 10.5[us]
X_acq_time	= 0.7293952[s]
X_angle	= 45[deg]
X_pulse	= 9.25[us]
Initial_wait	= 1[s]
Phase_preset	= 3[us]
Recvr_gain	= 23
Relaxation_delay	= 14[s]
Temp_get	= 25.1[dC]
Unblank_time	= 2[us]



153



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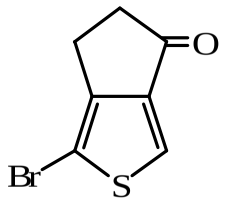
Author = delta
Experiment = single_pulse.exp
Sample_id = S#461760
Solvent = CHLOROFORM-D
Creation_time = 29-NOV-2007 17:54:52
Revision_time = 9-NOV-2008 19:35:53
Current_time = 9-NOV-2008 19:42:33

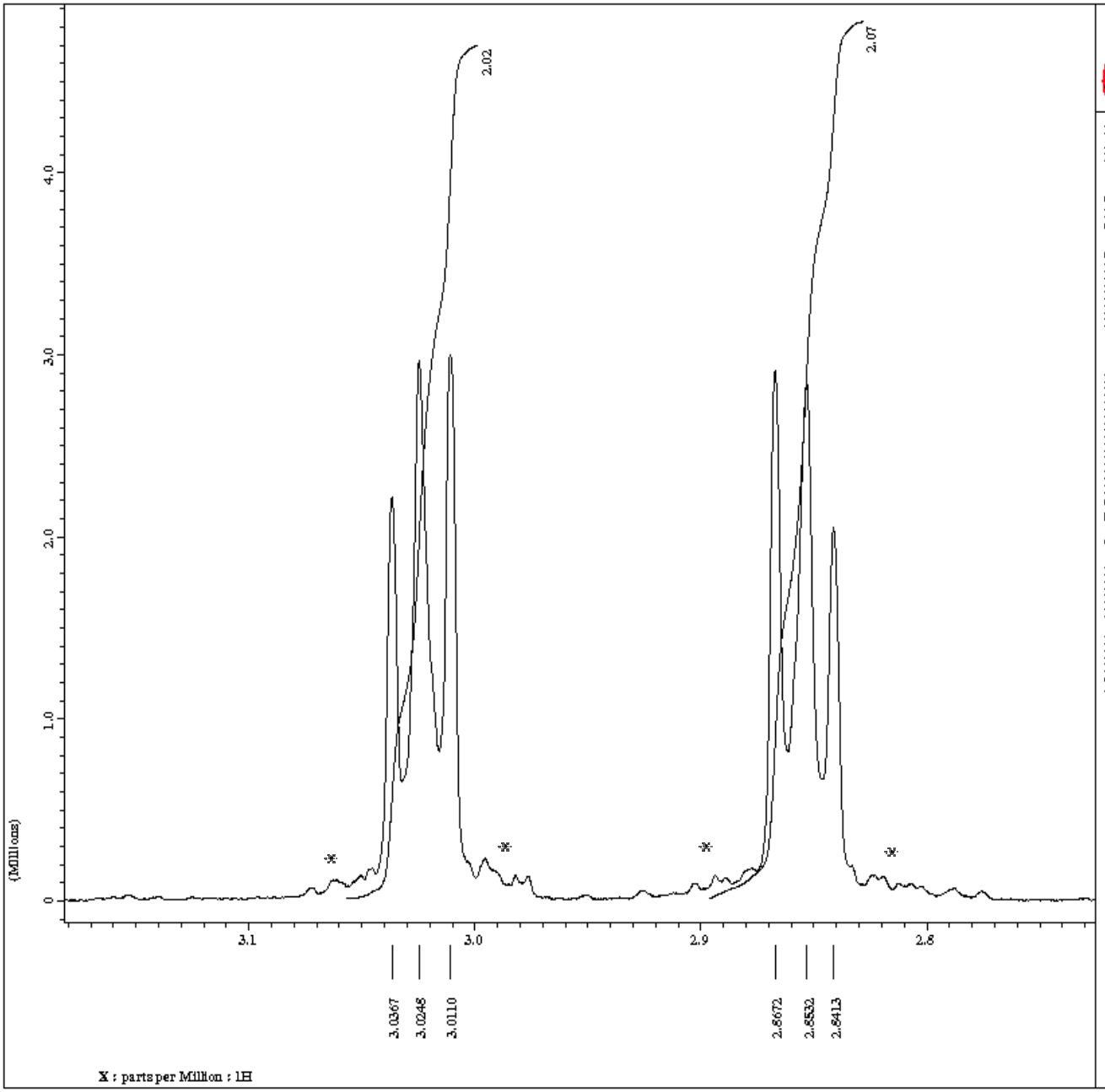
Comment = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 65536
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR

Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 0.7293952[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 65536
X_prescans = 0
X_resolution = 0.11455547[Hz]
X_sweep = 7.50750751[kHz]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8

X_90_width = 10.5[us]
X_acq_time = 0.7293952[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 23
Relaxation_delay = 14[s]
Temp_get = 25.1[dC]
Unblank_time = 2[us]



153



JEOL

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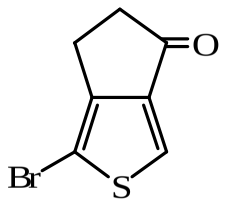
Filename          = 1-Br-CpTh-5.jdf
Author            = delta
Experiment        = single_pulse.exp
Sample_id         = S#461760
Solvent           = CHLOROFORM-D
Creation_time     = 29-NOV-2007 17:54:52
Revision_time     =  9-NOV-2008 19:35:53
Current_time      =  9-NOV-2008 19:44:26

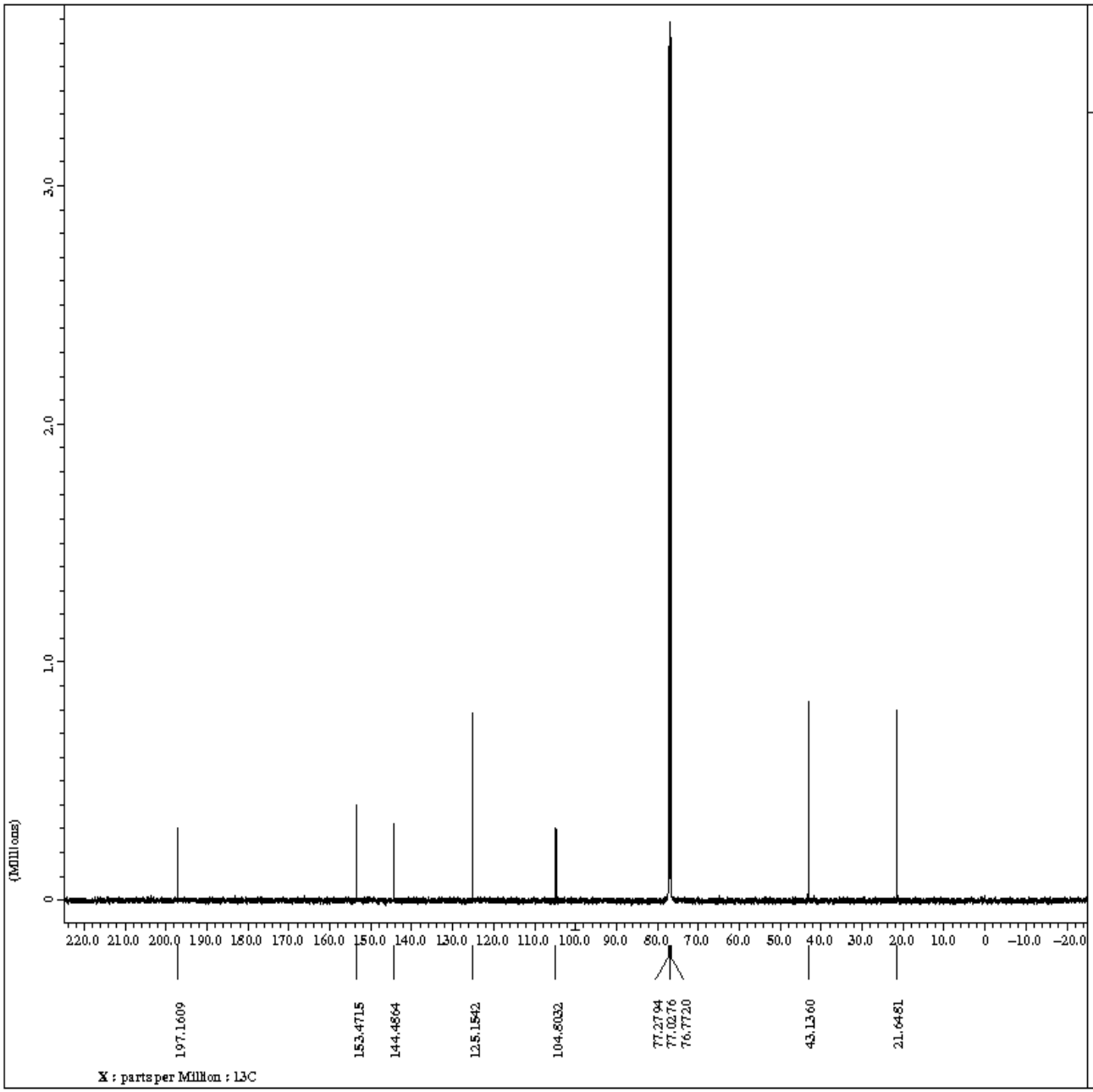
Comment           = Single Pulse Experime
Data_format       = 1D COMPLEX
Dim_size          = 65536
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

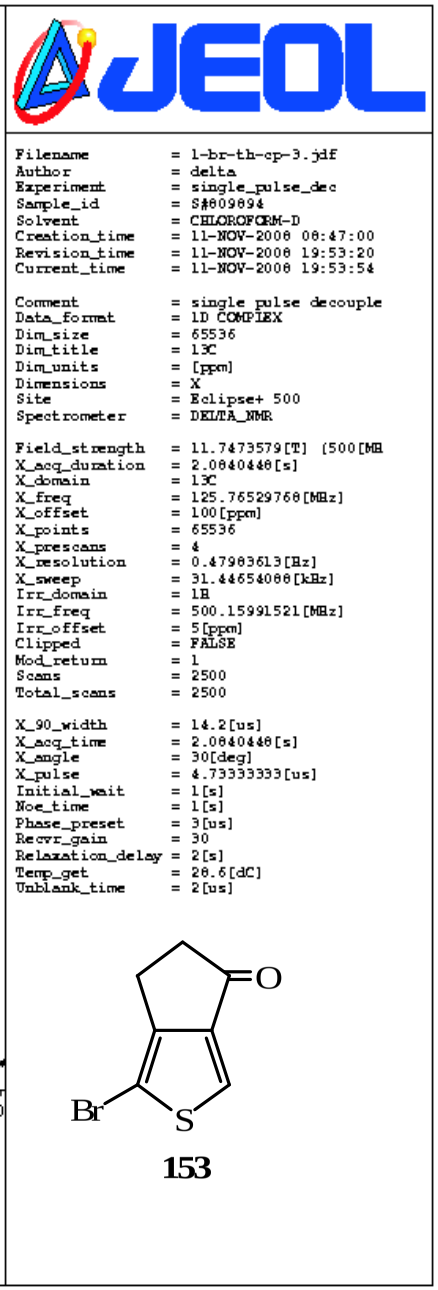
Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 0.7293952[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 5[ppm]
X_points          = 65536
X_prescans        = 0
X_resolution      = 0.11455547[Hz]
X_sweep           = 7.50750751[kHz]
Clipped           = FALSE
Mod_return        = 1
Scans             = 8
Total_scans       = 8

X_90_width        = 10.5[us]
X_acq_time        = 0.7293952[s]
X_angle           = 45[deg]
X_pulse           = 9.25[us]
Initial_wait      = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 23
Relaxation_delay  = 14[s]
Temp_get          = 25.1[dC]
Unblank_time      = 2[us]
```

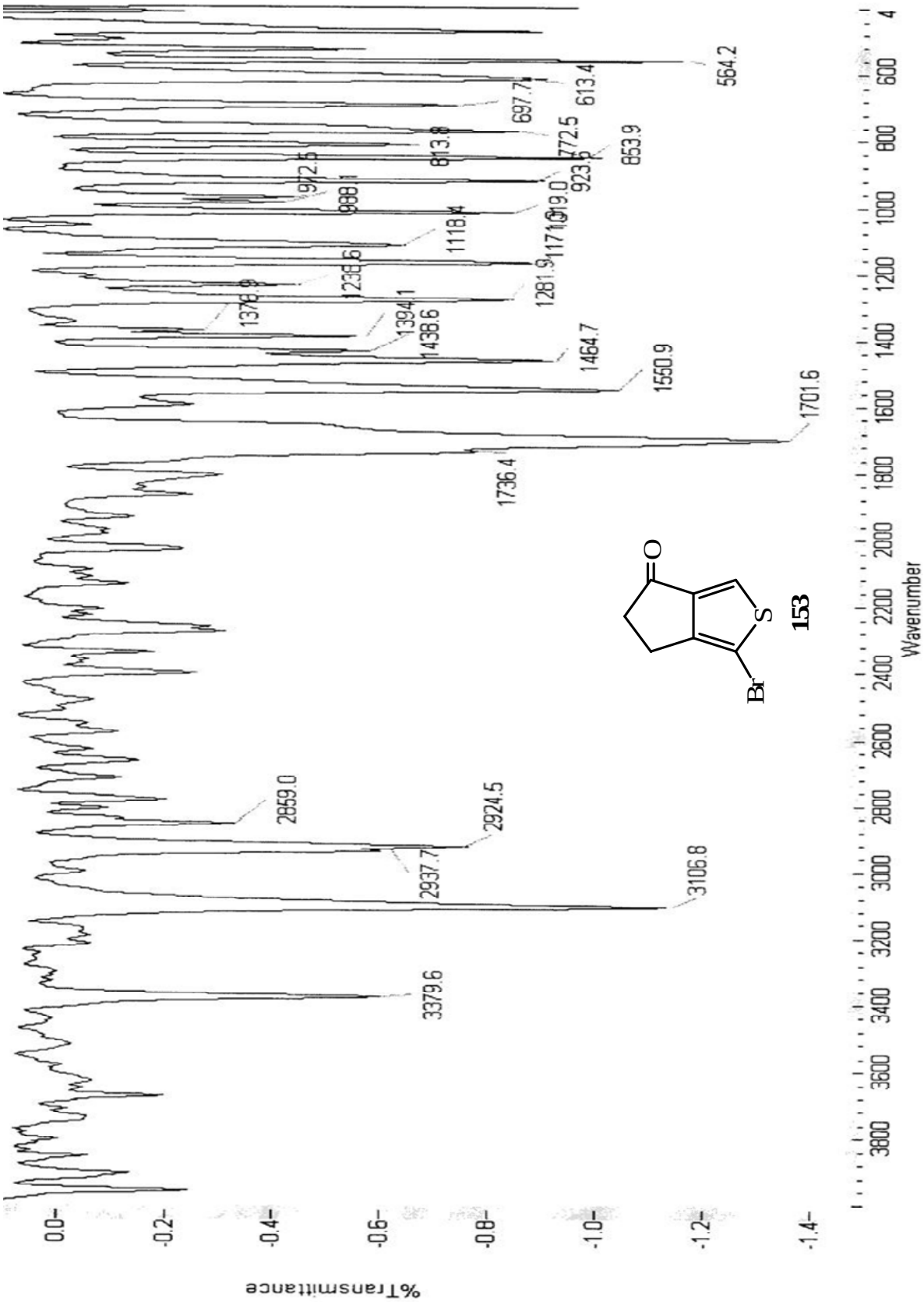


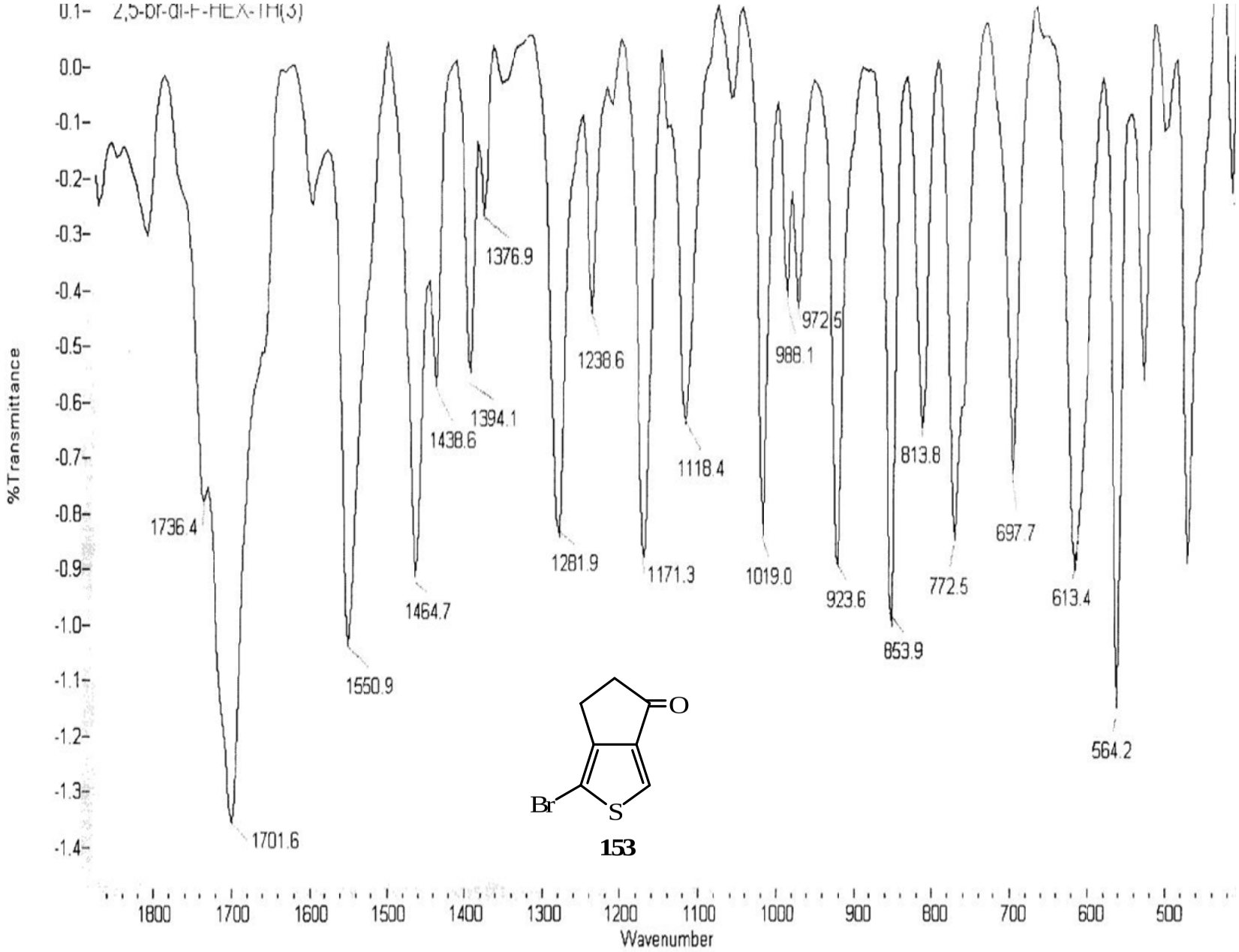
153


(Millions)
3.0
2.0
1.0
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 −10.0 −20.0
197.1609
153.4715
144.4864
125.1542
104.6032
77.2794
77.0276
76.7720
43.1360
21.6481
X : parts per Million : 13C


JEOL
Filename = 1-br-th-cp-3.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = S#809894
Solvent = CHLOROFORM-D
Creation_time = 11-NOV-2008 08:47:00
Revision_time = 11-NOV-2008 19:53:20
Current_time = 11-NOV-2008 19:53:54
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 65536
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.0840448[s]
X_domain = 13C
X_freq = 125.76529768[MHz]
X_offset = 100[ppm]
X_points = 65536
X_prescans = 4
X_resolution = 0.47983613[Hz]
X_sweep = 31.44654088[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 2500
Total_scans = 2500
X_90_width = 14.2[us]
X_acq_time = 2.0840448[s]
X_angle = 30[deg]
X_pulse = 4.73333333[us]
Initial_wait = 1[s]
Noe_time = 1[s]
Phase_preset = 3[us]
Recvr_gain = 30
Relaxation_delay = 2[s]
Temp_get = 28.6[dC]
Unblank_time = 2[us]
O
Br
S

153


%Transmittance
Wavenumber
3379.6
3106.8
2937.7
2924.5
2859.0
1736.4
1701.6
1550.9
1464.7
1438.6
1394.1
1376.9
1281.9
1238.6
1171.0
1118.4
1019.0
972.5
923.5
853.9
813.8
772.5
697.7
613.4
564.2
O
S
Br
153


2,5-Br-Cl-F-HEX-1H(3)
%Transmittance
Wavenumber
1736.4
1701.6
1550.9
1464.7
1438.6
1394.1
1376.9
1281.9
1238.6
1171.3
1118.4
1019.0
988.1
972.5
923.6
853.9
813.8
772.5
697.7
613.4
564.2
Br
S
O

153

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BIOGRAPHICAL INFORMATION

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